VOL. XX. JANUARY, 1898. NO. 1.

AMERICAN CHEMICAL JOURNAL

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON SALTS OF NITROPARAFFINS, AND ACYLATED DERIVATIVES OF HYDROXYLAMINE.

BY LAUDER W. JONES.

Of all the properties shown by the primary and secondary nitroparaffins, the two which seem to be the most characteristic are their tendency to form salts, and the peculiar power which they possess in the iso-form, either as salts or as esters, of producing oxidation-reactions. We are indebted chiefly to Nef[1] for our present conception of the salts. It was shown by him, that different constitutional formulæ must be assigned to the true nitro bodies and to their salts and esters, and that the metal or radical is bound to oxygen $\left(\begin{matrix} R—CH=N—O—M \\ \| \\ O \end{matrix}\right)$ and not to carbon; the discovery of isophenylnitromethane by Hantzsch and Schultze[2] confirms the work of Nef.

It was stated in the paper on the nitroparaffins, that the action of acid chlorides on the salts would be studied; that experiments with the yellow mercury salt obtained by the action of mercuric chloride on sodium isonitromethane, and attempts to synthesize esters of carbon dioxide oxime, R—O—N=C=O, would be continued. During the last

[1] Ann. Chem. (Liebig), **280**, 263. [2] Ber. d. chem. Ges., **29**, 699, 2251.

three years, I have carried out further investigations along these lines under the direction of Dr. Nef, and now present my results in detail.[1]

I. THE ACTION OF ACID CHLORIDES ON SODIUM ISONITROETHANE AND SODIUM ISONITROMETHANE.

1. *The Action of Benzoyl Chloride on Sodium Isonitroethane.*

The sodium isonitroethane used in the following experiments was prepared by adding sodium ethylate to an alcoholic solution of nitroethane. After filtering the salt, and washing thoroughly with alcohol and ether, it was carefully dried in a vacuum-desiccator to remove every trace of alcohol.

It was expected that the first product formed by the action of benzoyl chloride on sodium isonitroethane would be benzoylisonitroethane,

$$CH_3—CH=N(=O)—O—Na + C_6H_5—COCl =$$

$$CH_3—CH=N(=O)—O—CO—C_6H_5 + NaCl.$$

The reaction, however, is more complex in its nature, and benzoylisonitroethane undergoes a peculiar intramolecular oxidation, giving rise to an isomeric substance, the benzoyl ester of acethydroxamic acid.

$$CH_3—CH=N(=O)—O—CO.C_6H_5 \rightarrow CH_3—C(=N—O—COC_6H_5)—O—H.$$

This rearrangement furnishes a basis for the interpretation of the reaction. The benzoyl ester of acethydroxamic acid is a stronger acid than isonitroethane and decomposes sodium isonitroethane, setting free nitroethane, and forming the sodium salt of the benzoyl ester of the acethydroxamic acid,

$$CH_3—C(=N—O—CO.C_6H_5)—O—Na.$$

[1] A preliminary notice of my results, and a discussion of the formula proposed by Hantzsch for the nitroparaffin salts, were published by Dr. Nef in Ber. d. chem. Ges., 29, 1218.

In the presence of benzoyl chloride, this salt is converted into triacylated hydroxylamine derivatives, neutral substances, which constitute the chief products of the reaction.

Essentially the same results are obtained, with slight variations in the relative amounts of acid and neutral products, whether the reacting substances are dissolved in water or suspended in absolute ether. In each of the following experiments 20 grams of sodium salt were dissolved in 100 grams of water, and 28.8 grams of benzoyl chloride added; the table shows the relative quantities of acid and neutral products.

Experiment.	Soluble in $NaHCO_3$. Grams.	Soluble in NaOH. Grams.	Neutral Oil. Grams.
I.	6.5	3.2	12.3
II.	"	7.2	18.0
III.	6.5	7.0	16.5

Two experiments were performed, the substances being suspended in absolute ether: In Experiment I., 20 grams of sodium salt were suspended in 135 grams of absolute ether, and 28.8 grams of benzoyl chloride added; in Experiment II., 17.8 grams of sodium salt, 120 grams of absolute ether, and 25.0 grams of benzoyl chloride were used.

Experiment.	Soluble in $NaHCO_3$. Grams.	Soluble in NaOH. Grams.	Neutral. Grams.	Solid residue. Grams.
I.	4.7	3.5	19.3	13.5
II.	3.3	2.6	17.5	12.0

These two experiments were more favorable for a detailed study of the reaction than those carried out in water solution; they have been chosen as representative, and will be described in the account which follows.

17.5 grams of finely powdered sodium salt were suspended in 120 grams of absolute ether; the flask containing the mixture was placed in ice-water, and 25 grams (1 mol. = 25.7 grams) of benzoyl chloride were added in small portions. After standing a few minutes, the ether assumed a greenish hue, which finally passed into orange. The mixture was kept at 0° for two hours, and then allowed to stand at the temperature of the room, until the odor of benzoyl chloride was no longer noticeable.

The insoluble residue, removed by filtration, weighed 12

grams, and was composed chiefly of sodium chloride, with a small amount of sodium nitrite; no unchanged sodium isonitroethane was present.

The ether filtrate was placed in a distilling-bulb and subjected to distillation at reduced pressure; the distillate passed through a long, well-cooled condenser, and was caught in a receiver surrounded by a freezing-mixture. When most of the ether had passed off, the pressure was diminished to 130 mm., and the temperature of the water-bath increased to 75°; at 85°, the thick, yellow oil in the distilling-bulb began to turn red, and to prevent further decomposition, the distillation was interrupted. The small amount of colorless liquid, which accumulated in the receiver, gave, on redistilling, 2 grams of nitroethane, boiling at 113°–114°, which was identified by its properties, and by converting it into ethylnitrolic acid.

The oil remaining in the distilling-bulb, which still possessed a strong odor of nitroethane, was redissolved in ether, and the ether solution extracted, first with sodium bicarbonate (A), and then with dilute sodium hydroxide (B) (containing 10 grams of the hydroxide in 100 grams of water). The ether containing the neutral portion (C) was washed carefully with water, dried with calcium chloride, and the ether then allowed to evaporate in a vacuum-desiccator.

A. Portion Soluble in Sodium Bicarbonate.

Benzoyl ester of acethydroxamic acid, $CH_3—C(=O)—N(H)—O—COC_6H_5$.

—After acidifying the bicarbonate solution with dilute sulphuric acid, it was extracted with ether; 3.3 grams of crystalline material were obtained on evaporating the ether, which proved to be a mixture of two substances, benzoic acid, and the benzoyl ester of *acethydroxamic acid*.

A separation of these two substances was easily effected by treatment with boiling ligroïn (40°–60°), which readily dissolves benzoic acid. By this method the solid (3.3 grams) was separated into 2 grams of benzoic acid (melting-point 119°–

120°), and 1.3 grams of the benzoyl ester of acethydroxamic acid.

The latter exists in two forms: A part, 6.8 grams, was obtained by crystallizing from ether in large, well-developed crystals, melting at 98°–99°. The second form is more soluble in ether, and can be precipitated from ether, after the other form has crystallized out, by means of low-boiling ligroïn, in flat, transparent crystals, melting at 69°–70°. After standing for several days, this form becomes opaque, and in the course of a week or two passes completely into the high-melting form.[1] It is possible that this low-melting form is a hydroximic acid, $CH_3—C\begin{matrix}O—H\\ \diagdown\!\!\diagup\\ N—O—CO.C_6H_5\end{matrix}$, and that the change, which it undergoes on standing, is due to a rearrangement to form a hydroxamic acid, $CH_3—C\begin{matrix}O\\ \diagdown\!\!\diagup\\ NHOCO.C_6H_5\end{matrix}$.

0.1257 gram, melting at 98°–99°, gave 0.2793 gram CO_2, and 0.0593 gram H_2O.

0.1282 gram gave 9 cc. N_2 at 14° and 749 mm.

	Theory for $C_9H_9NO_3$.	Found.
C	60.33	60.27
H	5.02	5.15
N	7.83	8.16

Properties of the Benzoyl Ester of Acethydroxamic Acid.—It is readily soluble in alcohol, less soluble in chloroform, or ether, sparingly soluble in cold water, and almost insoluble in ligroïn, and benzol.

Towards alkalies it is quite sensitive, and is readily decomposed by them into benzoic acid and acethydroxamic acid, $CH_3—C\begin{matrix}O\\ \diagdown\!\!\diagup\\ N—HOH\end{matrix}$. Even boiling water causes the same decomposition, but much less readily. On heating, it is completely decomposed; benzoic acid, methyl isocyanate, and a brown residue are formed.

[1] By adding acid to a water solution of the sodium salt of the form melting at 98°–99°, and extracting with ether, a mixture of the two forms is obtained.

Sodium Salt, $CH_3-C(=N-O-CO.C_6H_5)-O-Na$.—By adding sodium ethylate to an alcoholic solution of the acid, and precipitating with absolute ether, a white, crystalline salt was obtained.

0.2582 gram gave 0.0843 gram Na_2SO_4.

	Theory for $C_9H_8NO_3Na$.	Found.
Na	11.43	11.46

This salt is readily soluble in water, and from this solution a white, non-crystalline silver salt can be precipitated by silver nitrate.

Synthesis of the Benzoyl Ester of Acethydroxamic Acid from Acethydroxamic Acid.—In order to establish the identity of the substance obtained from nitroethane, with the benzoyl ester of acethydroxamic acid, it was necessary to prepare this compound synthetically. 4 grams of acethydroxamic acid, $CH_3-C(=O)-NHOH$, (melting-point 88°–89°), prepared according to the method described by Miolati[1], were dissolved in 50 grams of water, and neutralized with 3 grams of potassium hydroxide in 25 grams of water. To this solution, well cooled, 7.5 grams of benzoyl chloride were added in small portions, shaking thoroughly after the addition of each portion. In a few minutes a dense, crystalline mass accumulated. This was collected on a filter, and pressed on a clay plate to remove water, and some unchanged benzoyl chloride. The dry product was treated with boiling ligroïn, which took up a small amount of benzoic acid.

This crude product (6.5 grams) was dissolved in ether. On standing, large, transparent crystals, melting at 98°-99°, were formed, which were identical in every respect with the substance obtained from nitroethane.

0.1796 gram, melting 98°–99°, gave 0.3975 gram CO_2, and 0.0842 gram H_2O.

0.2423 gram gave 16.9 cc. N_2 at 18° and 742.7 mm.

[1] Ber. d. chem. Ges., **25**, 700.

	Theory for $CH_3-C\overset{O}{\underset{NHOCO.C_6H_5}{<}}$	Found.
C	60.33	60.36
H	5.02	5.20
N	7.83	7.90

In this case, also, two forms were observed. Of the 6.5 grams, 4.6 grams melted at 98°–99°, while 1.8 grams separated in flat crystals, melting at 69°–70°.

The absolute identity of the substance obtained from nitroethane (melting-point 98–99°), with the benzoyl ester of acethydroxamic acid, is established by the identity of the crystalline forms.

For the following crystallographic data, I am indebted to Mr. Zirngiebl, who kindly carried out the measurements of these two substances in Prof. Groth's laboratory at Munich.

Crystal system: monoclinic.

$$a : b : c = 1.4623 : 1 : 1.4545$$

$$\beta = 94° 41'$$

The forms which were observed are: 001, 110, 101, $11\bar{1}$, 100; the last two are sometimes wanting.

$$001 : 100 = 85° 19'$$
$$001 : 101 = 42° 31'$$
$$110 : \bar{1}10 = 68° 43'$$

Cleavage completely in 001.

The plane of the optical axes $\perp$ 010.

B. Portion Soluble in Sodium Hydroxide.

The solution in sodium hydroxide possessed an intense red color, which disappeared on acidifying with dilute sulphuric acid, and was due, as will be shown, to the presence of salts of ethylnitrolic acid. By means of ether 2.6 grams of crystalline material were extracted. This solid proved to be a mixture of the following substances:

	Grams.
Benzoic acid,	1.9
Benzoyl ester of benzhydroxamic acid, $C_6H_5-C\overset{O}{\underset{NHO.CO.C_6H_5}{<}}$,	0.4

Benzoyl ester of acethydroxamic acid, $CH_3—C(=O)—NHOCO.C_6H_5$, traces.

Ethylnitrolic acid $CH_3—C(=NO_2)—N—O—H$, traces.

A separation of these substances was accomplished as follows: The entire residue (2.6 grams) was dissolved in the smallest possible amount of sodium hydroxide, and carbon dioxide conducted into the solution until no more benzoyl ester of benzhydroxamic acid (dibenzhydroxamic acid) separated. This substance was removed by filtration, and extraction with ether. Recrystallized from alcohol, it separated in fine needles, melting at 158°–159°. A portion was converted into the potassium salt, and this, by boiling with water, into diphenylurea (melting at 235°–236°).

A nitrogen determination was also carried out.

0.2968 gram gave 15.1 cc. N_2 at 16.5° and 756.8 mm.

	Theory for $C_{14}N_{11}NO_3$.	Found.
N	5.80	5.90

The filtrate was acidified, and the benzoic acid which separated, collected on a filter and dried. It melted at 117°–118°, and contained traces of the benzoyl ester of acethydroxamic acid.

The acidified solution, from which the benzoic acid had been removed, was neutralized with sodium hydroxide; to the deep-red solution a few drops of benzoyl chloride were added, and the mixture shaken until a yellow crystalline solid deposited. After recrystallizing from boiling alcohol, this solid melted at 134°–135°, and was identical with the benzoyl ester of ethylnitrolic acid, $CH_3—C(=NO_2)—N—O—CO.C_6H_5$, which melts at 135°. 0.4 gram was obtained.

These substances are undoubtedly formed by the decomposition of the neutral portion in the presence of sodium hydroxide. The formation of ethylnitrolic acid is explained by the presence of the benzoyl ester of ethylnitrolic acid,

$CH_3—C(NO_2)=NOCOC_6H_5$. When benzoyl chloride acts on sodium isonitroethane in water solution, larger amounts of this benzoyl compound are formed, and crystallize from the neutral oil on standing. Its presence is to be explained by a decomposition of sodium isonitroethane, with formation of nitrous acid; the green color, which the ether solution first assumes, points to this decomposition. Nitrous acid reacts with sodium isonitroethane to form ethylnitrolic acid, which is a stronger acid than isonitroethane, and decomposes sodium isonitroethane, forming the sodium salt of ethylnitrolic acid. This reacts with benzoyl chloride to form the benzoyl ester of ethylnitrolic acid. The formation of dibenzhydroxamic acid, $C_6H_5CO.NHOCOC_6H_5$, and the benzoyl ester of acethydroxamic acid will be explained, when the nature of the neutral portion is discussed.

C. Neutral Portion.[1]

Benzoyl Ester of Benzoylacethydroxamic Acid, $CH_3—C(O—COC_6H_5)=NOCOC_6H_5$, and *α-Benzoyl-β-acetylbenzoylhydroxylamine,* $(CH_3—CO)(C_6H_5—CO)N.O—CO—C_6H_5$.

After the ether and volatile portions had passed off, 17.5 grams of thick, reddish oil remained. When the amount of material taken is compared with the amount recovered, it becomes apparent that considerable loss has occurred.

	Taken. Grams.		Found. Grams.
Sodium isonitroethane,	17.8	Neutral,	17.5
Benzoyl chloride,	25.0	Acid,	5.9
		Solid residue,	12.0
	42.8	Nitroethane,	2.0
			37.4

Loss = 5.4 grams.

[1] The neutral oil is not, as was at first supposed, a mixture containing "Tribenzhydroxylamine," $C_6H_5C(OCOC_6H_5)=NOCOC_6H_5$, as one of its ingredients, but a mixture of the two isomers given above. *Vide* Ber. d. chem. Ges., **29**, 1218.

As no evolution of gas occurred, this loss must have been due to volatile liquid, and in view of the fact that nitroethane was recovered, and that the oil still possessed a strong odor of nitroethane, almost the entire loss must be attributed to regenerated nitroethane, except perhaps slight losses which occurred in extracting with sodium bicarbonate and sodium hydroxide.

The regenerated nitroethane would, on this basis, amount in all to 7.4 grams (5.4 grams + 2.0 grams), which is a little more than half of the nitroethane used.

7.4 grams of nitroethane = 9.5 grams of sodium isonitroethane.

One-half of the sodium salt used, 17.8 = 8.9 grams.

Properties of the Oil.—This oil showed no signs of solidifying in a freezing-mixture, and even after an exposure of several weeks to the extremest cold of winter weather, only a slight deposit was formed, and this redissolved on attempting to separate it from the oil.

It cannot be distilled, even under diminished pressure, without undergoing complete decomposition, with the formation of benzoic acid, acetic acid, an isocyanate, and a brown, non-volatile residue.

On warming a few drops of the oil with dilute alkali, it is decomposed; dilute sulphuric acid precipitates benzoic acid, and the acidified solution gives an intense reaction with ferric chloride, indicating the presence of hydroxamic acids.

The behavior of the oil towards concentrated hydrochloric acid, its behavior towards alcoholic potash, and an analysis show that it is a triacylated hydroxylamine derivative, to which the empirical formula, $(CH_3CO)(C_6H_5CO)_2ON$, must be assigned.

Behavior towards concentrated Hydrochloric Acid.—The oil is decomposed by concentrated hydrochloric acid into benzoic acid, acetic acid, and hydroxylamine hydrochloride, with traces of ammonium chloride.

5.0 grams were heated with 2–3 volumes of acid for two hours at 100° in a sealed tube. No pressure was observed on opening the tube.

The benzoic acid was filtered, washed once with ice-water, dried, and weighed. It was found to weigh 4.1 grams, while 4.3 grams is the amount calculated for $(CH_3CO)(C_6H_5CO)_2ON$.

The filtrate was diluted with water to a volume of 250 cc., and distilled until two-thirds of this volume had passed into the receiver. This distillate was treated with silver carbonate, heated to boiling, filtered, and evaporated to dryness on a water-bath. In this way 1.0 gram of silver acetate was obtained, which, after recrystallizing from hot water, and washing with absolute alcohol to remove traces of silver benzoate, gave the following figures on analysis:

0.1120 gram gave 0.0722 gram Ag.

	Theory for $CH_3—COOAg$.	Found.
Ag	64.66	64.46

The hydrochloric acid solution, which remained in the distilling-bulb, was evaporated to dryness in an evaporating-dish over a water-bath; 0.8 gram of the solid residue remained, consisting chiefly of hydroxylamine hydrochloride, with traces of ammonium chloride. It reduced Fehling's solution, and was converted into acetoxime; volatile, prismatic crystals were obtained, melting at 59°–60°.

Analysis.—The neutral oil, carefully washed with sodium bicarbonate and sodium hydroxide, and freed from volatile substances by standing *in vacuo* for two weeks, gave the following figures on analysis:

0.1658 gram gave 0.4175 gram CO_2, and 0.0690 gram H_2O.
0.1307 gram gave 0.3282 gram CO_2, and 0.0575 gram H_2O.
0.3407 gram gave 13 cc. N_2 at 21° and 748 mm.

	Theory for $(CH_3CO)(C_6H_5CO)_2ON$.	Found. I.	II.	III.
C	67.84	68.66	68.48	....
H	4.62	4.62	4.88	....
N	4.92	....	....	4.29

Considering the nature of the oil, and its method of preparation, the figures obtained agree well with the theory.

Behavior of the Oil towards Alcoholic Potash.

6.2 grams were dissolved in a few cubic centimeters of alco-

hol, and, after cooling the solution, 2.3 grams of potassium hydroxide (calculated 2 mol. = 2.4 grams), dissolved in a few grams of alcohol, were added. Almost immediately a crystalline salt formed, which increased on standing; after five minutes this salt was filtered from the deep-red alcoholic solution. It weighed 3.7 grams, and was composed of the potassium salts of benzoic acid and of the benzoyl ester of benzhydroxamic acid, $C_6H_5—C\begin{matrix}OK\\ \diagdown\\ \diagup\\ NOCOC_6H_5\end{matrix}$.

A separation of these two acids was accomplished by dissolving the mixture of the salts in water, and passing carbon dioxide through the solution. Thus 1.0 gram of the benzoyl ester of benzhydroxamic acid, melting at 158°–159°, was precipitated. It was also identified by converting it into diphenyl urea. On acidifying the filtrate, and extracting with ether, 1.6 grams of benzoic acid (melting-point 119°–120°) were obtained.

The original alcoholic solution was diluted with water and extracted with ether. 2.7 grams of the ethyl benzoate, boiling at 209°–212°, were obtained on distilling.

The solution was then acidified with dilute sulphuric acid, and extracted with ether. A solid, crystalline residue remained on evaporating the ether, which, recrystallized from ether and low-boiling ligroïn, gave 0.1 gram of the benzoyl ester of acethydroxamic acid, melting at 98°–99°, and 0.4 gram, melting at 69°–70°.

The presence of hydroxamic acids could be shown in the remaining solution by means of ferric chloride.

The results may be summed up as follows:

6.2 grams of oil gave:

	Grams.
Benzoyl ester of benzhydroxamic acid,	1.0
Benzoyl ester of acethydroxamic acid,	1.4
Benzoic acid,	1.6
Ethyl benzoate,	2.7

The formation of the benzoyl ester of acethydroxamic acid, $CH_3—CO.NH.CO.C_6H_5$, and benzoic acid (partially as ethyl

benzoate), can only be explained by the presence of the benzoyl ester of benzoylacethydroximic acid, $CH_3—C\begin{matrix}O.CO.C_6H_5\\ \diagdown\\ \diagup\\ NO.CO.C_6H_5\end{matrix}$, in the neutral oil. If the oil were made up entirely of this substance, it is impossible to account for the formation of the benzoyl ester of benzhydroxamic acid, $C_6H_5CONH.OCO.C_6H_5$. If, however, it is assumed that a triacylated hydroxylamine, constituted according to the true hydroxylamine type, *viz.*, $\begin{matrix}CH_3CO\\ C_6H_5CO\end{matrix}\!\!>\!N—O—CO.C_6H_5$, is also present, the formation of the benzoyl ester of benzhydroxamic acid becomes explicable, for of two groups bearing the same relation to the nitrogen atom, the acetyl group would be more readily affected by alcoholic potash than the benzoyl group.

The decomposition may be expressed thus :

$$CH_3—\overset{\overset{O}{\|}}{C}—OH. \qquad C_6H_5—\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{C}}—N—O—COC_6H_5.$$

In order to establish the correctness of this interpretation, it was necessary to study the action of benzoyl chloride on the sodium salt of the benzoyl ester of acethydroxamic acid, $CH_3—C\begin{matrix}ONa\\ \diagdown\\ \diagup\\ NOCOC_6H_5\end{matrix}$.

The Action of Benzoyl Chloride on the Sodium Salt of the Benzoyl Ester of Acethydroxamic Acid.

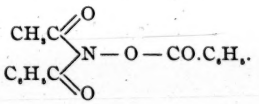
4.2 grams of the sodium salt, prepared as described above, were suspended in 38 grams of absolute ether, and 2.7 grams of benzoyl chloride (slightly less than 1 molecule) were added. The action commenced at once, and at the end of two days was complete.

The sodium chloride (1.2 grams) was filtered, and the ether solution evaporated ; a thick, colorless, syrupy oil remained in the evaporating-dish, weighing 5.4 grams. After standing for two weeks, exposed to the coldest winter temperature,

the oil showed signs of solidifying, and at the end of three weeks, the crystalline magma was transferred to a clay plate. The solid, freed from oil in this way, amounted to 2.5 grams. It was redissolved in a small quantity of ether, and warm ligroïn added, when, on cooling, it was deposited in large, transparent, well-developed crystals, melting at 68°–69°.

The oil was extracted from the pieces of clay plate by boiling ether; on evaporating the ether, a thick, oily substance remained, which showed no signs of solidifying after standing four weeks.

α-Benzoyl-β-acetylbenzoylhydroxylamine,



The solid, melting at 68°–69°, is a neutral substance, insoluble in alkalies, but decomposed by them quite readily. It is easily soluble in alcohol and ether, quite soluble in boiling ligroïn, sparingly soluble in cold ligroïn, and insoluble in water.

0.1327 gram gave 0.3307 gram CO_2, and 0.0560 gram H_2O.
0.1473 gram gave 6.8 cc. N_2 at 20° and 743.7 mm.

	Theory for $C_{16}H_{13}NO_4$.	Found.
C	67.84	67.95
H	4.62	4.68
N	4.94	5.15

The correctness of the formula assigned is shown by the behavior of the solid towards alcoholic potash, and more conclusively by its synthesis from the potassium salt of the benzoyl ester of benzhydroxamic acid and acetyl chloride, which will be considered later.

Behavior towards Alcoholic Potash.

The solid isomer is decomposed on treatment with alcoholic potash almost completely into the benzoyl ester of benz-

hydroxamic acid, $C_6H_5—C(=O)NHOCOC_6H_5$, and acetic acid (or acetic ether). Not a trace of the benzoyl ester of acet-hydroxamic acid, $CH_3—C(=O)NHOCOC_6H_5$, could be found.

1 gram of the crystalline isomer (melting-point 68°–69°) was dissolved in 20 grams of alcohol, and treated with alcoholic potash (0.4 KOH equivalent to 2 mols.). The crystalline salt which separated was filtered (0.4 gram), dissolved in water, and treated with carbon dioxide. In this way 0.38 gram of the benzoyl ester of benzhydroxamic acid, melting at 159°–160°, was obtained. It was identified by conversion into diphenylurea. The alcoholic filtrate was diluted with water, and extracted with ether. On distilling the ether extract, very small quantities of acetic ether, and benzoic ether were recognized by their odors. The diluted alcoholic solution was then acidified with dilute sulphuric acid; from this solution ether extracted 0.45 gram of the benzoyl ester of benzhydroxamic acid, containing traces of benzoic acid. This amount (0.45 gram), redissolved in sodium hydroxide and precipitated by carbon dioxide, gave 0.4 gram of pure acid, melting at 158°.

The acidified solution, from which these substances had been extracted, gave a reaction with ferric chloride for benzhydroxamic acid, $C_6H_5—CO.NHOH$, which was formed by the further decomposition of the benzoyl ester of benzhydroxamic acid; this explains the presence of traces of benzoic acid and benzoic ether.

In all, 0.76 gram of the benzoyl ester of benzhydroxamic acid were obtained instead of 0.85 gram, the calculated amount.

Benzoyl Ester of Benzoylacethydroxymic Acid,

$$CH_3—C(=N—O—CO—C_6H_5)O—CO.C_6H_5.$$

The oily isomer obtained in the above reaction shows a

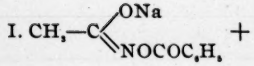
totally different behavior towards alcoholic potash. It is decomposed almost entirely into the benzoyl ester of acethydroxamic acid, $CH_3—C{=}O.NH.O.COC_6H_5$, and benzoic acid (or ethyl benzoate), which establishes the constitutional formula assigned. 0.9 gram of the oily isomer, treated with alcoholic potash (0.35 gram KOH in 17 grams alcohol) in exactly the same manner as the solid isomer, gave the following results:

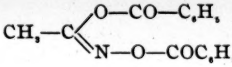
		Gram.
Benzoyl ester of acethydroxamic acid,	$CH_3—C(=O)NHOCOC_6H_5$	0.5
Ethyl benzoate,	$C_6H_5.COOC_2H_5$	0.3
Benzoic acid,	C_6H_5COOH	trace
Benzoyl ester of benzhydroxamic acid,	$C_6H_5—C(=O)NHOCOC_6H_5$	0.08

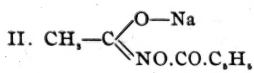
The formation of this last substance is to be accounted for by the presence of some of the solid isomer dissolved in the oil.

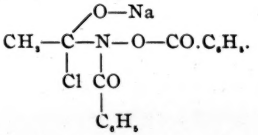
The neutral oil obtained from sodium isonitroethane, therefore, behaves in every respect as a mixture of almost equal quantities of these two isomers. It is not strange that this oil has resisted all attempts to solidify it, when we consider its method of preparation, and the fact that it contains slight impurities, such as ethyl benzoate and nitroethane. Furthermore, the product obtained by the action of the sodium salt of pure benzoyl ester of acethydroxamic acid and benzoyl chloride solidified but partially, and then only after an exposure of three weeks to extreme cold, accompanied by the usual scratching to facilitate crystallization.

It is only possible to explain the formation of the two isomers from the sodium salt of benzoyl ester of acethydroxamic acid and benzoyl chloride, by assuming that two processes are taking place side by side; namely, direct replacement of the metal by the benzoyl group, and the addition of benzoyl chloride to the sodium salt, with subsequent loss of sodium chloride.

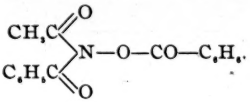
I.  + $C_6H_5CO.Cl$ =

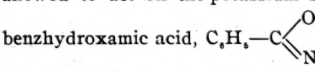
 + NaCl.

II.  + C_6H_5COCl =



By loss of sodium chloride the last product becomes



In order to establish the correctness of this explanation, the following experiment was carried out: Acetyl chloride was allowed to act on the potassium salt of the benzoyl ester of benzhydroxamic acid,  .

It is evident that if addition does occur, the addition-product formed in this case must be identical with the solid isomer (melting-point 68°–69°) obtained by the addition of benzoyl chloride to the sodium salt of the benzoyl ester of acethydroxamic acid. This conclusion is borne out by experiment.

The Action of Acetyl Chloride on the Potassium Salt of the Benzoyl Ester of Benzhydroxamic Acid, .—The benzoyl ester of benzhydroxamic acid used was pre-

pared according to Lossen's[1] method from hydroxylamine and benzoyl chloride.

11 grams of the potassium salt were suspended in absolute ether, and treated with 3.1 grams (1 mol.) of acetyl chloride. In twelve hours the action was complete. After removing the sodium chloride, the ether solution was placed in a glass evaporating-dish and the ether evaporated *in vacuo*. Thus, 8.2 grams of solid, crystalline material, with traces of oil, were obtained. The oil was removed by placing the solid on a clay plate, and was not investigated. The solid was crystallized as follows: Boiling ligroïn (40°–60°) dissolved it, with the exception of 0.5 gram of regenerated benzoylhydroxamic acid. On cooling, the ligroïn solution was filled with radiating groups of long, needle-shaped crystals, and at the same time short, thick, transparent crystals formed on the sides of the crystallizing flask. After filtering, these crystals were separated by selection. 3.7 grams of needle-shaped crystals, melting at 84°–85°, and 1.7 grams of transparent crystals, melting at 68°–69°, were obtained.

Solid Melting at 68°–69°.—This substance is identical in every respect with α-benzoyl-β-acetylbenzoylhydroxylamine, $\begin{matrix}CH_3CO\\C_6H_5CO\end{matrix}\!\!>\!N\!-\!O\!-\!CO.C_6H_5$, obtained from the benzoyl ester of acethydroxamic acid.

0.1443 gram gave 0.3583 gram CO_2, and 0.0610 gram H_2O.
0.2545 gram gave 11.2 cc. N_2 at 22° and 753.8 mm.

	Theory for $C_{16}H_{13}NO_4$.	Found.
C	67.84	67.75
H	4.62	4.69
N	4.94	4.96

Behavior towards Alcoholic Potash.—0.9 gram dissolved in 17 grams of alcohol, and treated with a solution of potassium hydroxide, containing 3.5 grams, gave 0.7 gram of the benzoyl ester of benzhydroxamic acid, $C_6H_5C\!\begin{matrix}=O\\-NHOCOC_6H_5\end{matrix}$; calculated 0.76 gram.

[1] Ann. Chem. (Liebig), **161**, 347.

A crystallographic comparison of crystals of this preparation with those obtained from the benzoyl ester of acethydroxamic acid and benzoyl chloride was carried out in Prof. Groth's laboratory at Munich by Mr. Zirngiebl, to whom I wish to express my obligation for his kindness. The complete identity of the two specimens is established.

Crystal system : monoclinic.

$$a : b : c = 1.3064 : 1 : 1.0390.$$

$$\beta = 107°22'.$$

The forms observed are : 010, 100, 001, $11\bar{1}$, $10\bar{1}$.

$$001 : 100 = 72°38'$$
$$\bar{1}11 : \bar{1}00 = 70°36'$$
$$\bar{1}11 : \bar{1}\bar{1}1 = 87°59'$$

Cleavage 001. Plane of the optical axes $\perp$ 010.

Benzoyl Ester of Acetylbenzhydroximic Acid,

$C_6H_5—C(O—CO.CH_3)=N—O—CO.C_6H_5$.—The solid, melting at 84°–85°, obtained in the same reaction, is formed by the direct replacement of the metal by the acetyl group. It is a neutral substance, soluble in ether, and alcohol, very slightly soluble in cold ligroïn, quite readily in warm ligroïn, and insoluble in water.

0.0602 gram gave 0.1494 gram CO_2, and 0.0265 gram H_2O.
0.2240 gram gave 9.7 cc. N_2 at 25° and 749.7 mm.

	Theory for $C_{16}H_{13}NO_4$.	Found.
C	67.84	67.68
H	4.62	4.88
N	4.94	4.79

The following equations will explain the formation of these substances :

I. $C_6H_5-C(OK)=NOCOC_6H_5 + CH_3COCl =$

$$C_6H_5-C(O-CO.CH_3)=N-O-CO.C_6H_5 + KCl.$$

II. $C_6H_5-C(OK)=N-O-CO.C_6H_5 + CH_3-COCl =$

$$C_6H_5-C(OK)(Cl)-N(CO.CH_3)-O-CO.C_6H_5.$$

This addition-product loses potassium chloride giving

$$C_6H_5C(=O)-N(-OCOC_6H_5)-C(=O)CH_3.$$

These reactions seem to throw some light upon the nature of the triacylated hydroxylamine derivatives in general. It has been established that compounds of this class exist in more than one form; in no case, however, in more than three forms. Lossen[1] has preferred to regard them as physical isomers, not, however, denying the possibility of considering them as space isomers. Hantzsch and Werner suggested the possibility of interpreting them from the standpoint of geometrical isomerism, depending upon the presence of an oxime grouping. Werner[2] has since established the presence of such isomeric relations among the hydroximic acid derivatives, as, for example, α- and β-ethylhydroximic acid, which he showed to be related as *syn* and *anti* forms,

$$C_6H_5-C(=N-O-H)-O-C_2H_5 \qquad C_6H_5-C(=N-O-H)-O-C_2H_5.$$

[1] Ann. Chem. (Liebig), **186**, 1; **252**, 170; **265**, 176; **281**, 169.
[2] Ber. d. chem. Ges., **25**, 27; **26**, 1562, 1567; **29**, 1153.

This, however, accounts for only two forms, and in some cases three are known. It has often been suggested that the third form may correspond to a true hydroxylamine type, $\begin{matrix}RCO\\RCO\end{matrix}\!\!>\!N\!-\!O\!-\!COR$; but experimental evidence was lacking to confirm this view. The results, presented above, prove conclusively that compounds of this type can exist. It still remains to be determined whether even this explanation is sufficient to account for all the cases of isomerism, and the many intricate relations observed in the study of the hydroxamic and hydroximic acids.

Explanation of the Reaction of Benzoyl Chloride with Sodium Isonitroethane.

Having considered this reaction in all its details, it is now possible to sum up the results, and to formulate the course of the action in the following equations. By the direct replacement of the metal by benzoyl, a derivative of isonitroethane results :

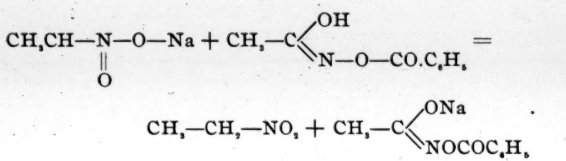
$$CH_3\!-\!CH\!=\!N\!-\!O\!-\!Na + C_6H_5\!-\!COCl =$$
$$\qquad\qquad\qquad\quad \| \quad O$$

$$CH_3\!-\!CH\!=\!N\!-\!O\!-\!CO.C_6H_5 + NaCl.$$
$$\qquad\qquad\quad \| \quad O$$

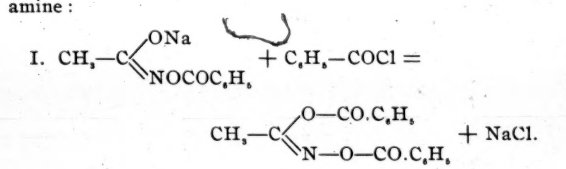
This substance cannot be isolated, but is immediately converted by intramolecular oxidation into the benzoyl ester of acethydroxamic acid,

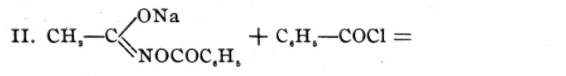
$$CH_3\!-\!CH\!=\!N\!-\!O\!-\!CO.C_6H_5 \rightarrow CH_3\!-\!C\!\begin{matrix}OH\\ \|\\ N\!-\!O\!-\!CO.C_6H_5\end{matrix}$$
$$\qquad\qquad\quad \| \quad O$$

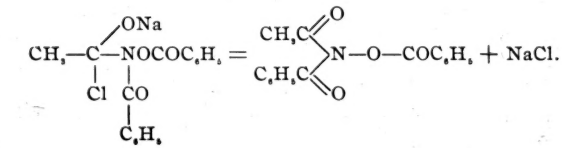
Being a stronger acid than isonitroethane, it immediately reacts with the isonitroparaffin salt, regenerating nitroethane, and forming the sodium salt of the benzoyl ester of acethydroxamic acid,



In the presence of benzoyl chloride, this salt reacts just as the synthetic salt was found to act, namely, in two ways, by addition; and by direct replacement, forming dibenzoylacethydroximic acid, and α-benzoyl-β-acetylbenzoylhydroxylamine:







2. *The Action of Chlorcarbonic Ether on Sodium Isonitroethane.*

This reaction has not been studied as thoroughly as the action of benzoyl chloride on sodium isonitroethane. The evolution of large amounts of carbon dioxide introduces a complication which was not foreseen, and although the resulting neutral oil contains derivatives of acethydroxamic acid, it has not been found possible to determine the exact nature of these substances.

22.3 grams of chlorcarbonic ether were allowed to act on 20 grams of sodium isonitroethane, suspended in 120 grams of

absolute ether; 3.2 grams of carbon dioxide were evolved, and a residue remained which weighed 16.9 grams, and was composed of sodium chloride (66 per cent.), sodium carbonate, and some sodium nitrate. The ether gave, on evaporation, 11.2 grams of reddish, neutral oil. A loss of material had occurred amounting to 11 grams; this was due chiefly to nitroethane, and amounts to a little more than half of the sodium nitroethane used.

Properties of the Neutral Oil.—It is sparingly soluble in water. On heating a few drops with sodium hydroxide and acidifying with dilute sulphuric acid, an evolution of carbon dioxide occurred, and ferric chloride gave an intense cherry-red color reaction, identical with the test given by acethydroxamic acid. When alkalies are added to the oil, the red color characteristic of salts of ethylnitrolic acid is produced; this disappears on acidifying, and is regenerated by fresh alkali.

After standing for several weeks, the oil showed no signs of solidifying. It suffers considerable decomposition when distilled even under diminished pressure. When distilled at ordinary pressure, a portion passes over below 170°; the remainder between 200° and 230°. Carbon dioxide is evolved, and the distillate possesses an intense odor of isocyanate. A few drops of the higher-boiling fraction, heated with alkali, gave, on acidifying, an intense reaction with ferric chloride; this shows that the derivatives of acethydroxamic acid distilled, at least in part, without decomposition.

Synthesis of the Carbethoxyl Ester of Acethydroxamic Acid, $CH_3—C(=O)—N(H)—O—CO_2C_2H_5$.—It was expected that the action of chlorcarbonic ether on sodium isonitroethane would give results corresponding to those obtained by the action of benzoyl chloride. It was necessary, therefore, to become familiar with the carbethoxy derivatives of acethydroxamic acid, and of ethylnitrolic acid. These have been prepared synthetically.

Six grams of acethydroxamic acid were dissolved in a few

cubic centimeters of cold water, and, after neutralizing with one molecule of potassium hydroxide, one molecule of chlorcarbonic ether was added. In a few minutes the reaction was complete; the clear solution was extracted with ether, the ether dried with calcium chloride, and partially distilled. The remainder, poured into an evaporating-dish, left, on evaporation, a snow-white crystalline mass, which, after drying on a clay plate to remove traces of chlorcarbonic ether, weighed 4.1 grams. Crystallized from ether and ligroïn (40°–60°), it separates in long, flat needles, with a shining, pearly luster, and melts at 71°–72°.

0.2700 gram gave 0.4039 gram CO_2, and 0.1507 gram H_2O.
0.1875 gram gave 15.2 cc. N_2 at 13°.5 and 756.4 mm.

	Theory for $C_5H_9NO_4$.	Found.
C	40.81	40.79
H	6.12	6.20
N	9.52	9.53

Properties of the Carbethoxyl Ester of Acethydroxamic Acid.— It is readily soluble in ether, alcohol, and water, soluble in benzol, and chloroform, almost insoluble in ligroïn. A water solution, when first prepared, gives no reaction with ferric chloride, but on standing several hours it shows an intense color reaction. It is readily decomposed by alkalies, and alkaline carbonates, acethydroxamic acid being formed. Towards acids it is much more stable.

Its behavior on distillation resembles, in some respects, the behavior of the neutral oil obtained by the action of chlorcarbonic ether on sodium isonitroethane; carbon dioxide is evolved, an intense odor of isocyanate is observed, and a pale yellow oil distils between 180°–220°.

Synthesis of the Carbethoxyl Ester of Ethylnitrolic Acid,

$CH_3—C(NO_2)=N—O—CO_2C_2H_5$.—2.4 grams of the ethylnitrolic acid, prepared from nitroethane, were dissolved in 25 cc. of water; 0.9 gram of potassium hydroxide, and 2.5 grams of chlorcarbonic ether were added. The red color of the solution soon disappeared, and a yellow oil separated.

The solution and yellow oil were extracted with ether, the ether dried with calcium chloride, and distilled; 2.1 grams of the oil were obtained by distillation at reduced pressure, boiling at 143°–144° under 17 mm.

0.1720 gram gave 0.2187 gram CO_2, and 0.0719 gram H_2O.

	Theory for $C_5H_8N_2O_5$.	Found.
C	34.09	34.67
H	4.54	4.64

Properties.—It is a pale yellow oil, slightly soluble in water. Boiling water decomposes it, liberating carbon dioxide, and forming ethylnitrolic acid and its decomposition-products. In the presence of alkalies, it is readily decomposed, an intense red solution of salts of ethylnitrolic acid being formed. It boils at ordinary pressures, with considerable decomposition, at 210°–215°.

The presence of this substance in the neutral oil obtained by the action of chlorcarbonic ether on sodium nitroethane, accounts for the formation of salts of ethylnitrolic acid, on treating this oil with alkalies.

3. *The Action of Benzoyl Chloride on Sodium Isonitromethane.*

This reaction still presents difficulties, which have not been overcome. The action seems to proceed in a different manner, depending upon the kind of salt used, that is, whether the alcoholate, $CH_2{=}NONa,C_2H_5OH$, or the alcohol-free salt is

$$CH_2{=}N(=O)ONa$$

used.

In all cases, the chief product of the reaction is a neutral oil.

20 grams of the sodium isonitromethane[1] (alcohol-free) and 33

[1] A curious observation in this connection with nitromethane may be mentioned here. Kahlbaum's nitromethane was used, and its purity established by distillation. It was perfectly transparent, and free from color when first obtained; but, on exposure to the light for some time, it gradually assumed a pale yellow tinge, and an odor identical with that of *prussic acid* was noticed. Could this have been due to the formation of fulminic acid, H—O—N=C, by oxidation:

$$H_2C{-}NO_2+H_2O=H_2C{-}N(=O)OH=H_2C{=}N(=O)OH+H_2O?$$

This isonitromethane, by intramolecular oxidation, could yield formhydroximic acid, and this, by loss of water, fulminic acid:

$$H_2C{=}N(=O)OH=HC(OH){=}NOH=C{\equiv}N{-}OH+H_2O.$$

grams of benzoyl chloride in 180 grams of absolute ether, gave 19.8 grams of reddish, neutral oil. The solid residue weighed 17.2 grams, and contained, in addition to sodium chloride, a considerable quantity of sodium benzoate. The sodium bicarbonate, and sodium hydroxide extracts gave 5.3 grams of benzoic acid. A loss, therefore, of 10.7 grams of material had occurred, which was due to regenerated nitromethane.

Properties of the Neutral Oil.—The oil could not be solidified. Complete decomposition ensued on attempting to distil it, even at reduced pressure; benzoic acid, and isocyanate were formed. Concentrated hydrochloric acid decomposed it, forming large quantities of benzoic acid (3 grams of oil gave 2.6 grams of benzoic acid), small amounts of formic acid (identified as lead salt), and some hydroxylamine hydrochloride (identified as acetoxime). When heated with dilute alkalies, it suffers decomposition; benzoic acid is deposited on acidifying, and the solution gives an intense reaction with ferric chloride, identical with the color reaction obtained with formhydroxamic acid, $H-C(=O)-NHOH$, which has been synthetically prepared, and will be described later.

Behavior towards Alcoholic Potash.—6 grams of this neutral oil, treated with alcoholic potash in the manner described in connection with the neutral oil obtained from nitroethane, gave 3.2 grams of potassium benzoate, 2.5 grams of ethyl benzoate, 1 gram of benzoic acid, and 0.3 gram of the benzoyl ester of formhydroxamic acid, $H-C(=O)-NHOCO.C_6H_5$. The mixture of benzoic acid and the benzoyl ester of formhydroxamic acid extracted from the acidified alcoholic solution by ether was treated with boiling ligroïn to remove benzoic acid, and the remaining benzoyl ester of formhydroxamic acid purified by recrystallizing from ether and ligroïn. It separated in transparent crystals, melting at 76°–77°, identical with the crystals of this substance prepared synthetically from formhydroxamic acid and benzoyl chloride, which will be described in connection with formhydroxamic acid.

The formation of this substance, by the action of alcoholic potash on the neutral oil, confirms the presence of the benzoyl ester of benzoylformhydroxamic acid in the oil. It is, therefore, evident that the action of benzoyl chloride on sodium nitromethane proceeds, at least in part, according to the following equations:

$$H_2C{=}N{-}ONa + C_6H_5{-}COCl = H_2C{=}N{-}O{-}CO.C_6H_5.$$
$$\quad\quad\quad

zoyl chloride on sodium isonitromethane would be benzoyl derivatives of formhydroxamic acid.

In order to become familiar with the properties of these substances, it was necessary first to prepare synthetically formhydroxamic acid, the simplest of the hydroxamic acids.

Formhydroxamic Acid, $H-\overset{\overset{O}{\|}}{C}-N(H)-OH$.—A brief mention is made by Miolati[1] of a copper salt of formhydroxamic acid, but he does not describe any attempts to isolate the free acid. After several trials, the following method of preparation has been found to be the most satisfactory :

30 grams of hydroxylamine hydrochloride were dissolved in 150 cc. of boiling methyl alcohol, and to this solution, still warm, a solution of sodium methylate, containing 9.9 grams of sodium, was added. After mixing, the flask was cooled, and finally allowed to stand in a freezing-mixture for some time. The sodium chloride was filtered off, and the alcoholic solution of hydroxylamine distilled at reduced pressure, until two-thirds of the alcohol had distilled over.

After removing a small amount of sodium chloride, which had been deposited during the distillation, by filtering through glass wool, the solution was cooled to 0°, and 31 grams of formic ether added directly. A slight elevation in temperature was observed, which was moderated by shaking, and cooling with running water. After standing for several hours at the temperature of the room, the mixture was placed in a glass evaporating-dish, and the methyl alcohol removed by evaporating in a vacuum-desiccator. 20 grams of crystalline material, containing some oil, and a slight amount of sodium chloride remained. The oil was removed by pressing the residue on a clay plate. Thus 17.9 grams of almost pure formhydroxamic acid were obtained, which was freed from the small quantity of sodium chloride by dissolving in pure ethyl acetate (free from acetic acid and water), heated to a temperature near its boiling-point. If

[1] Ber. d. chem. Ges., **25**, 703.

heated too long, or too high, much decomposition results.

On cooling, pure formhydroxamic acid, melting at 81°–82°, separated in large, thin, transparent plates, with a brilliant, pearly luster, and striated surfaces.

0.1890 gram gave 0.1359 gram CO_2, and 0.0847 gram H_2O.

0.1765 gram gave 35.8 cc. N_2 at 17° and 743.4 mm.

	Theory for $H-C\langle^{O}_{NHOH}$.	Found.
C	19.67	19.60
H	4.91	4.98
N	22.95	23.09

Properties of Formhydroxamic Acid.—It is insoluble in chloroform, ligroïn, and benzol; very slightly soluble in ether; readily soluble in alcohol, and water. It is dissolved by warm acetone, and is deposited on cooling in groups of thick crystals. On standing in contact with acetone, however, these crystals redissolve, and suffer a decomposition, the nature of which has not been fully determined. If perfectly pure formhydroxamic acid is required, it can be prepared best by using pure hydroxylamine, obtained by distillation according to the method of Lobry de Bruyn, instead of the concentrated alcoholic solution containing sodium chloride. A water solution of formhydroxamic acid, even in the presence of considerable mineral acid, gives an intense cherry-red color reaction with ferric chloride, differing very slightly in tint from the color obtained with acethydroxamic acid.

The pure acid is quite stable, is not hygroscopic, and can be kept in open vessels without decomposition; in closed tubes, it soon undergoes decomposition. When heated to a temperature slightly above its melting-point, it explodes with a sudden puff, sending forth a cloud of vapor, possessing the peculiar odor of hydroxylamine. This decomposition seems to be due to a dissociation into carbon monoxide and free hydroxylamine:

$$H-C\langle^{O}_{NHOH} = CO + H_2NOH.$$

The stability of this substance is best explained by assign-

ing to it the oxam formula, $H-C\begin{matrix}O\\ \diagdown\\ NHOH\end{matrix}$; if the oxime form, $H-C\begin{matrix}OH\\ \diagdown\\ NOH\end{matrix}$, were correct, this substance would lose water spontaneously, and give fulminic acid :

$$\begin{matrix}HO\\ \diagdown\\ H\end{matrix}\!\!>C=NOH = H_2O + C=NOH,$$

just as the oxime of formyl chloride, $\begin{matrix}Cl\\ \diagdown\\ H\end{matrix}\!\!>C=NOH$, was found to lose hydrochloric acid. It is, therefore, very probable, that the hydroxamic acids in the free state are constituted according to the oxam, and not according to the oxime type.[1]

Sodium Salt.—A sodium salt is formed by adding to an alcoholic solution of the acid one molecule of sodium ethylate. The alcohol must be absolute, otherwise the salt will separate as a gummy mass. A precipitate is first formed, which redissolves on adding the entire amount of sodium ethylate. This is probably an acid salt. From the alcoholic solution, the sodium salt is precipitated by adding absolute ether as a fine, white powder. The filtration and washing must be carried out very rapidly, as the salt is extremely hygroscopic. No analysis was made. Heated on a spatula, the salt explodes with a sharp puff, and a yellow flame. Salts are precipitated from its water solution by copper acetate, mercuric chloride, and lead acetate.

The copper salt is a dark green powder. The lead salt separates as a white, crystalline powder, which explodes on heating. The mercury salt, a deep yellow powder, explodes by percussion and on heating.

The Action of Benzoyl Chloride on the Salts of Formhydroxamic Acid.

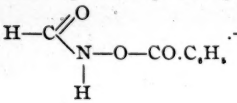
To a solution of 10 grams of formhydroxamic acid in 50

[1] The study of formhydroxamic acid, and its derivatives, especially in their relation to and conversion into fulminic acid and its esters, RON=C, will be continued in this laboratory.—J. U. Nef.

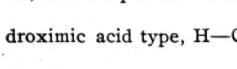
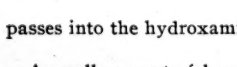
grams of cold water (5°), a solution of 6.5 grams of sodium hydroxide in 25 grams of water was added, and then benzoyl chloride, in small portions, until 23.3 grams were used. During the reaction the temperature was kept at 5°, and the flask shaken from time to time. A thick, gummy mass separated, and floated on the surface of the water. After shaking for ten minutes, the mixture was transferred to a separatory-funnel, and extracted with ether. Neutral and acid products were obtained by shaking the ether-extract first with a solution of sodium bicarbonate, then with a solution of sodium hydroxide. The remaining ether contained the neutral portion. The original water solution, after extraction with ether, gave an intense reaction with ferric chloride, showing the presence of large amounts of unchanged formhydroxamic acid.

Soluble in Sodium Bicarbonate.

Benzoyl Ester of Formhydroxamic Acid,



.—On acidifying the solution in sodium bicarbonate with dilute sulphuric acid, a colorless oil was formed. This was taken up by ether, the ether dried with calcium chloride, and evaporated; 7 grams of solid residue (no oil!) remained.

It is possible that in this case, also, two forms exist; the oil, which separated on acidifying, may correspond to the hydroximic acid type,  , which readily passes into the hydroxamic acid form,  .

A small amount of benzoic acid was removed by boiling ligroïn, and the remaining solid, 5.5 grams, which melted at 55°–60°, was dissolved in 50 cc. of absolute ether. On cooling, it crystallized in well developed, prismatic crystals, melting at 76°.5–77°.5. By addition of ligroïn it is completely precipitated from ether solution.

0.1250 gram gave 0.2662 gram CO_2, and 0.0487 gram H_2O.
0.1710 gram gave 12.9 cc. N_2 at 21° and 753 mm.

	Theory for $C_8H_7NO_3$.	Found.
C	58.18	58.08
H	4.24	4.32
N	8.48	8.54

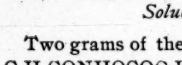
Properties of the Benzoyl Ester of Formhydroxamic Acid.—It is readily soluble in alcohol, less soluble in ether, almost insoluble in ligroïn, and sparingly soluble in water. By sodium hydroxide it is decomposed, slowly in the cold, readily on warming, into formhydroxamic acid and benzoic acid. Heat decomposes it; benzoic acid distils, and an intense odor of isocyanate is observed. The substance is identical with the benzoyl ester of formhydroxamic acid, obtained from nitromethane.

Soluble in Sodium Hydroxide.

Two grams of the benzoyl ester of benzhydroxamic acid, $C_6H_5CONHOCOC_6H_5$, (melting at 159°–160°), were obtained from the acidified solutions. Its formation is to be accounted for by the partial decomposition of formhydroxamic acid into carbon monoxide and hydroxylamine.

Neutral Portion.

Benzoyl Ester of Benzoylformhydroximic Acid,

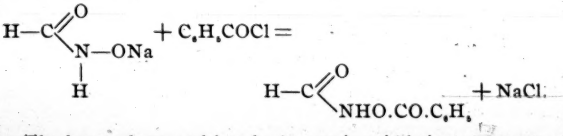


.—Most of the ether was removed by distillation. On pouring the remainder into an evaporating-dish, 7.5 grams of crystalline solid separated. Recrystallized from warm ether and ligroïn, it was obtained in delicate, colorless needles, melting at 109°–111°.

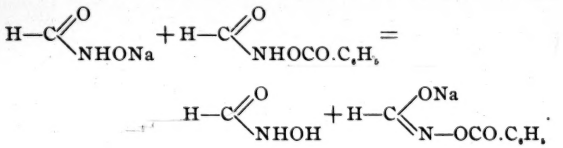
0.1407 gram gave 0.3443 gram CO_2, and 0.0553 gram H_2O.
0.2539 gram gave 12.2 cc. N_2 at 25° and 745 mm.

	Theory for $C_{15}H_{11}NO_4$.	Found.
C	66.91	66.74
H	4.08	4.36
N	5.20	5.28

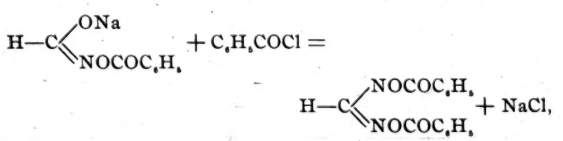
Properties. — It is quite readily soluble in warm ether, and sparingly in cold ether, slightly soluble in warm ligroïn, and insoluble in water. It is insoluble in alkalies, but is decomposed by them, more readily on warming than in the cold. On acidifying, benzoic acid separates, and the solution gives an intense reaction with ferric chloride for formhydroxamic acid. The reaction may be represented by the following equations :



The benzoyl ester of formhydroxamic acid being a stronger acid than formhydroxamic acid, decomposes the sodium salt of the latter, setting free formhydroxamic acid,



This sodium salt then reacts with benzoyl chloride,

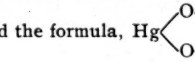


to give the benzoyl ester of benzoylformhydroximic acid.

Experiments with the Mercury Salt Obtained by the Action of Mercuric Chloride on Sodium Isonitromethane.

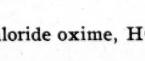
83 grams of sodium isonitromethane were dissolved in water, and, after cooling to 0°, a cold solution containing 121 grams of mercuric chloride was added. After standing two days, the white precipitate, which was at first deposited, be-

came yellow; it was boiled twice with water, filtered, and dried carefully on a clay plate. The product weighed 105 grams.

Many fruitless experiments were carried out with the salt and alkyl iodides. The mercury salt was supposed to be a basic mercury salt of carbon dioxide oxime, H—O—N=C=O, to which Nef assigned the formula,  . It was hoped that esters of this acid, R—O—N=CO, would result.

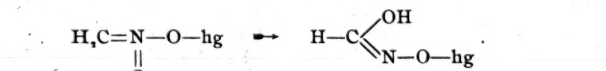
A peculiar odor resembling that of prussic acid was observed by Nef, on treating this salt with dilute hydrochloric acid. In order to determine the nature of this substance, 10 grams of the mercury salt were heated with the calculated amount of dilute hydrochloric acid, and an attempt made to distil the volatile substance, and collect it in a well-cooled receiver. The yellow color of the salt disappeared, and a gray residue remained, weighing 3 grams. When a small portion of this residue was heated on a spatula, it exploded exactly like mercuric fulminate. It was redissolved in a solution of potassium cyanide, and precipitated, by adding dilute nitric acid, as a crystalline powder, identical with mercuric fulminate.

The original yellow salt is also soluble in potassium cyanide, but, if dilute nitric acid is added rapidly, not a trace of fulminate is obtained. It is, however, possible, by adding nitric acid drop by drop, to obtain mercuric fulminate from the solution of the salt in potassium cyanide.

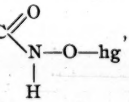
The peculiar odor observed on treating the salt with dilute hydrochloric acid is due, therefore, to small quantities of formyl chloride oxime,  .

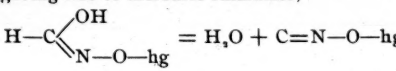
In view of the experiments with acid chlorides and isonitroparaffin salts, which have led, in all cases, to the formation of hydroxamic acid derivatives, it seems likely that, in the action of mercuric chloride on sodium isonitromethane, derivatives of formhydroxamic acid may be formed, as intermediate prod-

ucts in the synthesis of fulminates, discovered by Nef.[1] Thus,[2]

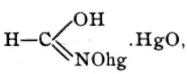
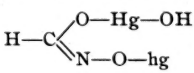


By oxidation,

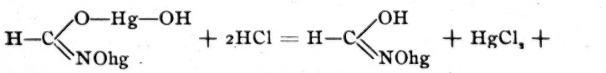
This salt of a hydroximic acid, before it can readjust itself to form a salt of a hydroxamic acid,  , loses water, giving rise to mercuric fulminate,

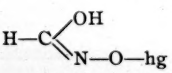


At the same time, by the further action of mercuric chloride, a basic mercury salt of formhydroximic acid results,

 or 

It is evident that on treating this basic salt with dilute hydrochloric acid, mercuric fulminate must be formed.





[1] Ann. Chem. (Liebig), 280, 270. [2] hg represents a half atom of bivalent mercury.

	Theory for $H-C(=NOhg)-O-Hg-OH$	Found.
C	3.2	3.34
H	0.53	0.305
N	3.7	4.04
Hg	79.7	80.31

This interpretation is offered tentatively. It may be mentioned that a yellow mercury salt has been obtained by the action of mercuric chloride on the sodium salt of formhydroxamic acid, which resembles, in many respects, the peculiar salt described above. Both explode violently on heating, and by percussion.

The above experiments prove, in any case, that the yellow basic salts obtained from nitromethane cannot be derivatives of carbon dioxide oxime, as was considered probable by Nef; their behavior towards sodium amalgam, and other reagents, makes it improbable that they are basic fulminates. Their conversion into fulminates, as shown above, makes it possible to convert sodium isonitromethane almost quantitatively into mercuric fulminate.

Concerning the Formula of the Salts of the Nitroparaffins.

In assigning to the isonitroparaffins the open formula, $R-\underset{\underset{H}{|}}{C}=\underset{\underset{O}{||}}{N}-OH$, and excluding the ring grouping of Hantzsch, $R-\underset{\underset{O}{\vee}}{\overset{\overset{H}{|}}{C}}-N-OH$,[1] it was pointed out by Nef[2], that the latter formula does not explain the peculiar property, which these bodies possess, of undergoing intramolecular oxidation.

Many instances can be cited in which formulæ containing ring groupings have been assumed arbitrarily for which there is no experimental evidence. As examples of this kind, the following may be mentioned:

[1] Ber. d. chem. Ges., **29**, 699, 2251. [2] *Ibid.*, **29**, 1218.

Nitrous oxide, $N{=}N{\overset{\vee}{O}}$ instead of $N{\equiv}N{=}O$.

Azoxy bodies, $R{-}N{=}N{\overset{\vee}{O}}R$ instead of $R{-}N{=}N{-}R$.
$\quad\quad\quad

nitrous oxide, by the action of dilute acid, observed by Nef.[1]

Examples of the second class have been described by Nef.[2] Dinitroethane silver, $CH_3—\underset{\underset{NO_2}{|}}{C}=\underset{\underset{O}{||}}{N}—O—Ag$, on treatment with alkyl iodides, gives results which can only be explained by admitting the formation of an ester, $CH_3—\underset{\underset{NO_2}{|}}{C}=\underset{\underset{O}{||}}{N}—O—R$, which then decomposes, giving an aldehyde, and ethylnitrolic acid,

$$CH_3—\underset{\underset{NO_2}{|}}{\overset{}{C}}=\underset{\underset{O}{||}}{N}—O—CH_2—R \rightarrow CH_3—\underset{\underset{NO_2}{|}}{C}=N—O—H + R—C\overset{O}{\diagdown\!\!\diagup H}$$

in the manner described by Nef. Another instance is found in the ethyl ester of fulminuric acid,

$$N\equiv C—\underset{\underset{C=O.NH_2}{|}}{C}=\underset{\underset{O}{||}}{N}—O—C_2H_5 \rightarrow$$

$$N\equiv C—\underset{\underset{CONH_2}{|}}{C}=N—O—H + CH_3—C\overset{O}{\diagdown\!\!\diagup H},$$

which, on boiling with water, gives acetic aldehyde, and cyanisonitrosoacetamide.

It is impossible to see how these reactions are to be interpreted, if the ring grouping is adhered to.

II. Carbethoxyhydroxamic Acid (Oxyurethane), $C_2H_5O—C\overset{O}{\diagdown\!\!\diagup NHOH}$, and its Alkyl and Acyl Derivatives.

In connection with the study of the mercury salt described above, attempts were made to obtain derivatives of the oxime of carbon dioxide, HO—N=C=O, from the salts and esters

[1] Ann. Chem. (Liebig), **280**, 266.
[2] *Ibid.*, **280**, 266.

of carbethoxyhydroxamic acid. If the salts possessed the form assigned by Lossen to the hydroxamic acids, $C_2H_5O-C(OH)=N-OM$, it seemed possible that under certain conditions they would lose alcohol, and give rise to salts of the oxime of carbon dioxide. Many attempts were made to remove this alcohol, but without success.

The monoalkyl esters of carbethoxyhydroxamic acid were then prepared, $C_2H_5O-C(=O)-NHOR$ ($R = CH_3$, C_2H_5, C_3H_7), and preliminary experiments with these compounds have been carried out. It was expected that under the influence of phosphorus pentachloride, these esters would be decomposed, yielding hydrochloric acid, an alkyl chloride, and esters of the oxime of carbon dioxide, R—ON=C=O. These esters have not yet been isolated, but are undoubtedly formed in this way.

Carbethoxyhydroxamic Acid (*Oxyurethane*), $C_2H_5O-C(=O)-NHOH$.—This substance was first prepared by Hantzsch,[1] who obtained it by the action of hydroxylamine, in water solution, on chlorcarbonic ether, in the presence of sodium carbonate. The following modification of this method has been used, and found to give more satisfactory yields:

19.5 grams of hydroxylamine hydrochloride were finely powdered, and placed in a flask with 38 grams of powdered dry potassium carbonate. Enough ether was added to more than cover the mixture, and a few cubic centimeters of water. 30 grams of chlorcarbonic ether were then poured into the flask, a small portion at a time; the flask was cooled, and shaken until the violent solution of carbon dioxide moderated, and permitted the addition of another portion of chlorcarbonic ether. When the entire amount had been used, the flask was allowed to stand, being shaken from time to time, until the evolution of carbon dioxide ceased. The potassium

[1] Ber. d. chem. Ges., 27, 1254.

chloride was removed by filtration, the ether was washed once with water, dried with dehydrated sodium sulphate, and the ether distilled; 26 grams of carbethoxyhydroxamic acid were obtained, equal to 89.6 per cent. of the theoretical yield.

Properties.—Prepared in this way it is identical with the oxyurethane described by Hantzsch.[1] It is a thick, colorless liquid, extremely soluble in water, and gives with ferric chloride an intense color reaction. On distillation, it was almost completely decomposed; at 180°–185° a colorless liquid distilled, which, on cooling, solidified to a mass of large, transparent plates, melting at 49°–50°. These were found to be urethane, $O=C\begin{smallmatrix}NH_2\\OC_2H_5\end{smallmatrix}$, (melting-point 49°–51°, boiling-point 184°).

Sodium Salt of Carbethoxyhydroxamic Acid, $C_2H_5-O-C\begin{smallmatrix}O\\NHONa\end{smallmatrix}$. H_2O.—By adding sodium ethylate to an alcoholic solution of the acid, a sodium salt is precipitated as a white, crystalline powder, which detonates when heated to 110°.

0.2474 gram gave 0.1288 gram of Na_2SO_4.

0.2974 gram gave 0.1470 gram of Na_2SO_4.

	Theory for $C_3H_4NO_3Na + H_2O$.	Found. I.	Found. II.
Na	15.86	16.8	16.0

This salt is readily soluble in water, and its solution reduces silver nitrate in the cold, and Fehling's solution on warming.

The Action of Methyl Iodide on Salts of Carbethoxyhydroxamic Acid.

To a solution of 29 grams of carbethoxyhydroxamic acid in methyl alcohol, a solution of 15.4 grams of potassium hydroxide in methyl alcohol, and 42 grams of methyl iodide were added. The separation of potassium iodide commenced at once, and it became necessary to cool the flask to prevent too great an elevation of temperature. After standing twenty-

[1] *Loc. cit.*

four hours, the potassium iodide was removed, and the methyl alcohol distilled under reduced pressure. The oil which remained, was dissolved in ether, and separated into neutral and acid portions by extracting the ether solution with dilute sodium hydroxide.

Soluble in Sodium Hydroxide.

Methyl Ester of Carbethoxyhydroxamic Acid,

$C_4H_7O{-}C(=O){-}NHOCH_3$.—After acidifying the alkaline extract with dilute sulphuric acid, it was shaken out with ether, the ether dried and distilled. 9.2 grams of colorless liquid, boiling at 186°–188°, were obtained.

0.1372 gram gave 0.2047 gram CO_2, and 0.0953 gram H_2O.
0.2092 gram gave 21.7 cc. N, at 17° and 749.1 mm.

	Theory for $C_4H_9NO_3$.	Found.
C	40.33	40.61
H	7.56	7.70
N	11.76	11.90

Properties.—It is readily soluble in ether, alcohol, and water. When perfectly pure, it gives no reaction with ferric chloride, but traces of carbethoxyhydroxamic acid are sometimes present in the acid portion, and are carried over with the oil. In this case a reaction with ferric chloride is obtained, and the methyl ester is rendered impure by the presence of traces of urethane.

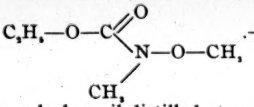
Decomposition by Concentrated Hydrochloric Acid.—1.4 grams of the methyl ester were heated with 10 cc. of concentrated acid in a sealed tube for an hour. On opening the tube, carbon dioxide and ethyl chloride escaped. The acid solution, evaporated to dryness on a water-bath, gave a crystalline residue, which dissolved completely in absolute alcohol. It was precipitated by absolute ether in white, crystalline flakes, melting at 148°–149°, identical in every respect with α-methylhydroxylamine hydrochloride, $CH_3ONH_2.HCl$, which melts at 149°.

0.0538 gram gave 0.0917 gram AgCl.

	Theory for CH_3ONH_2HCl.	Found.
Cl	42.51	42.46

Neutral Portion.

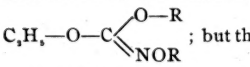
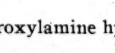
α-Methyl-β-Methylcarbethoxyhydroxylamine,



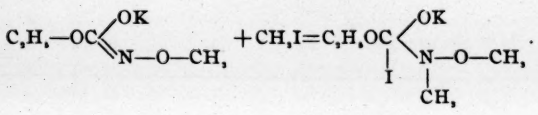
.—When the ether had passed off, a colorless oil distilled at 150°–155°, weighing 4 grams. The neutral portion is formed in larger amounts when 2 molecules of potassium hydroxide, and 2 molecules of methyl iodide, are used; thus 22.5 grams of carbethoxyhydroxamic acid, 24 grams of potassium hydroxide, and 63 grams of methyl iodide, gave 2 grams of acid oil, methyl ester of carbethoxyhydroxamic acid, boiling at 186°–188°, and 10.5 grams of neutral oil. In all cases considerable decomposition occurs.

A nitrogen determination showed that the oil was impure. 0.2410 gram (150°–153°) gave 19 cc. N_2 at 19° and 742 mm.

	Theory for $C_4H_{11}NO_3$.	Found.
N	10.52	8.88

The nature of this impurity has not been determined. It was at first expected that the neutral oil would contain alkyl derivatives of the carbethoxyhydroxamic acid of the form,  ; but the decomposition of the oil by concentrated hydrochloric acid shows that the oil consists chiefly of α-methyl-β-methylcarbethoxyhydroxylamine, for not α-methylhydroxylamine hydrochloride, CH_3ONH_2HCl, but α-dimethylhydroxylamine hydrochloride,  . HCl is formed.

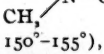
In order to explain this reaction, we must assume that the alkyl iodide acts with the potassium salt of the methyl ester of carbethoxyhydroxamic acid by addition, and not by direct replacement.



This product then loses potassium iodide, giving rise to α-methyl-β-carbethoxymethylhydroxylamine.

Decomposition of the Neutral Oil by Concentrated Hydrochloric Acid.

α-Dimethylhydroxylamine Hydrochloride,



.HCl.—Two grams of the oil (boiling-point 150°–155°), were heated in a sealed tube to 100° for thirty minutes with 10 cc. of concentrated hydrochloric acid. On opening the tube, carbon dioxide and ethyl chloride escaped. A crystalline salt, weighing 0.8 gram remained on evaporating the hydrochloric acid solution to dryness on a water-bath. The salt was soluble in alcohol, and precipitated from this solution by absolute ether, in small, shining plates, melting at 115°–116°. The best method of purifying it consists in dissolving the residue in boiling chloroform, from which it crystallizes, on cooling, in long, coarse, prismatic needles, melting at 115°–116°.

0.1209 gram gave 0.1086 gram CO_2, and 0.0894 gram H_2O.
0.1980 gram gave 24.5 cc. N, at 20° and 750.7 mm.
0.2097 gram gave 0.3057 gram of AgCl.
0.1049 gram gave 0.1555 gram of AgCl.

	Theory for	Found.	
C	24.61	24.49	
H	8.20	8.21	
N	14.35	14.37	
Cl	36.41	35.71	36.65

Properties of α-Dimethylhydroxylamine Hydrochloride.—This salt is not hygroscopic, does not reduce ammoniacal silver nitrate; Fehling's solution is not reduced. It is quite volatile at the temperature of the water-bath, and considerable loss

occurs on evaporating its solution to dryness. The same similarity in solubility is noticed in the case of α-methylhydroxylamine and α-dimethylhydroxylamine hydrochlorides, that has been observed with the methylamine and dimethylamine hydrochloride; that is, the dimethyl derivatives in each case are soluble in chloroform, while the monomethyl derivatives are not.

α-Dimethylhydroxylamine Chlorplatinate, $(CH_3NHOCH_3)_2 \cdot PtCl_4$.—By adding platinic chloride, dissolved in alcohol, to an alcoholic solution of the hydrochloride, a solution of the chlorplatinate was obtained. Absolute ether precipitates the chlorplatinate as a deep orange-colored powder, melting with decomposition at 180°. It is obtained in red, prismatic crystals on recrystallizing from alcohol.

0.1341 gram gave 0.0510 gram Pt.

	Theory for $(CH_3ONHCH_3)_2PtCl_4$.	Found.
Pt	38.92	38.04

α-Dimethylhydroxylamine, $\begin{matrix} H \\ CH_3 \end{matrix}\!\!>\!N\!-\!O\!-\!CH_3$.—Two grams of the hydrochloride, 5 grams of potassium hydroxide, and 10 grams of water, were placed in a small distilling-bulb, connected with a tube containing pieces of potassium hydroxide, and heated to 80° on a water-bath. The tube was connected with a condenser, through which ice-water circulated during the distillation. The free base (1 gram) was caught in a small distilling-bulb, cooled in a freezing-mixture, and redistilled, the same precautions being taken to cool the vapor. It boiled at 42°.2–42°.6.

0.1791 gram gave 0.2548 gram CO_2, and 0.1815 gram H_2O.

0.0734 gram gave 15.4 cc. N_2 at 19° and 737.8 mm.

	Theory for $\begin{matrix} H \\ CH_3 \end{matrix}\!\!>\!N\!-\!O\!-\!CH_3$.	Found.
C	39.34	38.80
H	11.47	11.26
N	22.95	23.50

Properties of α-Dimethylhydroxylamine.—It is a colorless, extremely volatile liquid, possessing a sweet, rather unpleas-

ant basic odor, not in the least ammoniacal. It does not reduce silver nitrate or Fehling's solution. This furnishes a method for preparing the α-dialkylhydroxylamines in a state of purity, and avoids all of the difficulties encountered in their preparation from α-monoalkylhydroxylamines by the action of alkyl iodides.[1]

The study of these derivatives of carbethoxyhydroxamic acid will be continued, with a view to preparing simple and mixed α-dialkylhydroxylamines.

The Action of Ethyl Iodide on the Salts of Carbethoxyhydroxamic Acid.

Twenty grams of carbethoxyhydroxamic acid, dissolved in absolute alcohol, were treated with 10.7 grams of potassium hydroxide, and 30 grams of ethyl iodide. After standing for fifteen hours, the mixture was heated for ten minutes to a temperature of 80°–90°, and, after cooling, filtered. The residue was not pure potassium iodide, but contained some potassium nitrite, and potassium carbonate.

The alcoholic solution was diluted with water, and extracted with ether. The acid portion was removed from the ether by means of dilute sodium hydroxide; the neutral products remained dissolved in the ether.

Soluble in Sodium Hydroxide.

Ethyl Ester of Carbethoxyhydroxamic Acid,

$C_2H_5—O—C(=O)—NHOC_2H_5$.—After acidifying the alkaline solution, it was extracted with ether, and the ether dried with calcium chloride. On distilling, 10 grams of the acid oil were obtained, boiling at 195°–196° (95°–97° at 17 mm.).

0.1412 gram gave 0.2313 gram CO_2, and 0.1029 gram H_2O.
0.1615 gram gave 0.2651 gram CO_2, and 0.1208 gram H_2O.
0.1883 gram gave 18.5 cc. N_2 at 24° and 742.5 mm.

	Theory for $C_6H_{11}NO_3$.	Found. I.	II.	III.
C	45.11	44.67	44.77	....
H	8.27	8.09	8.30	....
N	10.52	....	....	10.82

[1] Lossen: Ann. Chem. (Liebig), **252**, 235.

Properties.—It is readily soluble in water, alcohol, and ether. Concentrated hydrochloric acid decomposes it; carbon dioxide is evolved, ethyl chloride, and α-ethylhydroxylamine hydrochloride are formed. The latter substance was precipitated from its alcoholic solution by ether in shining, pearly scales, melting at 127°–128°, which were found to be identical with α-ethylhydroxylamine hydrochloride prepared synthetically.

0.2597 gram gave 0.3825 gram AgCl.

	Theory for $C_2H_5ONH_2HCl$.	Found.
Cl	36.41	36.67

Action of Phosphorus Pentachloride on the Ethyl Ester of Carbethoxyhydroxamic Acid.—It was hoped that esters of the oxime of carbon dioxide, RON=C=O, would be formed by this means, but owing to the instability of the reaction-product, it has not been possible to decide whether esters of this form are present or not; the behavior of the product, however, seems to point to their presence.

On mixing the oil with phosphorus pentachloride, the action commences at once, and is greatly facilitated by gentle heat. Hydrochloric acid and ethyl chloride are evolved in large quantities, and a yellow oil remains in the distilling-bulb, mixed with phosphorus oxychloride. An attempt was made to distil this oil; when the oxychloride had passed off, and the thermometer still stood at 110°–115°, the liquid in the distilling-bulb began to turn brown, and with an enormous evolution of heat, passed into a dark-brown, carbonaceous residue.

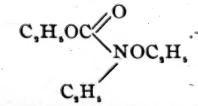
If the reaction-product was poured directly into water, without attempting to distil it, a decomposition took place, carbon dioxide was evolved, and a clear solution resulted, from which only a few drops of oil could be extracted by ether. The water solution was made strongly alkaline by adding sodium hydroxide, and distilled, the distillate passing into a receiver containing dilute hydrochloric acid.

On evaporating the acid solution, almost the calculated amount of α-ethylhydroxylamine hydrochloride was obtained. Thus 5 grams of the ethyl ester of carbethoxyhydroxamic acid

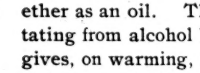
gave 2.1 grams of hydroxylamine salt instead of 2.6 grams. This shows conclusively that the ethyl chloride evolved was not produced by the ethoxy group bound to nitrogen, but must have been formed by the ethoxy group bound to carbon. The study of this reaction will be continued.

Neutral Portion.

α-Ethyl-β-Ethylcarbethoxyhydroxylamine,



.—As in the case of the neutral methyl derivative, the ethyl derivative is impure. On evaporating the ether, an oil was obtained which boiled between 160° and 180°. Owing to the small amounts of this oil which have been prepared, a separation of the mixture by fractional distillation has not been tried. Its behavior towards concentrated hydrochloric acid shows that it consists essentially of the above compound, for not α-ethylhydroxylamine, but α-diethylhydroxylamine hydrochloride is found. The substance remains on evaporating the hydrochloric acid solution to dryness as a yellow oil, soluble in alcohol, and reprecipitated by ether as an oil. The same result was obtained on precipitating from alcohol by ligroïn. With dilute sodic hydrate it gives, on warming, a strong basic odor. It does not reduce Fehling's solution or ammoniacal silver nitrate. After standing in a desiccator in the cold for several weeks, it solidified partially to a mass of long, fibrous needles, which, after recrystallization from alcohol and ether, melted at 123°–124°.

The oily salt behaves just as α-diethylhydroxylamine hydrochloride,  , which has never, until now, been obtained in the solid form.[1]

The Action of Benzyl Chloride on Carbethoxyhydroxamic Acid Salts.

27 grams of the carbethoxyhydroxamic acid, 11.9 grams of

[1] Lossen: Ann. Chem. (Liebig), **252**, 235.

potassium hydroxide, and 31 grams of benzyl chloride were dissolved in alcohol. Potassium chloride was deposited at once, and it was necessary to cool the flask, containing the mixture, to prevent too great a rise of temperature. After fifteen hours, the potassium chloride was removed by filtration, and after diluting the alcoholic solution with water, it was extracted with ether. The ether solution was shaken with dilute sodium hydroxide to remove acid products.

Soluble in Sodium Hydroxide.

Benzyl Ester of Carbethoxyhydroxamic Acid.

$C_6H_5—O—C(=O)NHO—CH_2C_6H_5$.—On acidifying the alkaline extract with dilute sulphuric acid, a light, colorless oil separated, and floated on the surface of the solution. This was extracted with ether, the ether dried and distilled. The residue was subjected to distillation at reduced pressure; 17 grams of colorless oil distilled at 171°–172° under 11 mm. pressure.

0.1562 gram gave 0.3523 gram CO_2, and 0.0958 gram H_2O.
0.2245 gram gave 13.9 cc. N_2 at 18° and 754.7 mm.

	Theory for $C_{15}H_{15}NO_3$.	Found.
C	61.53	61.51
H	6.61	6.82
N	7.18	7.13

Properties.—It is a thick, colorless oil, almost insoluble in water, readily soluble in alcohol and ether. It is soluble in alkalies, and is precipitated undecomposed by acids. On distilling at ordinary pressure, it suffers partial decomposition; a slight odor of benzaldehyde was observed.

Potassium Salt.—By adding alcoholic potash to an alcoholic solution of the acid, and precipitating with ether, the salt is obtained as a white, crystalline powder. It does not fuse at 260°. Heated in a tube, it decomposes, forming volatile, aromatic oils.

Sodium Salt.—The sodium salt was prepared by the action of sodium ethylate on an alcoholic solution of the acid. This

salt is much more soluble in alcohol than the potassium salt, and is not precipitated by ether.

The alcoholic solution was evaporated in a vacuum-desiccator; a colorless liquid remained, which redissolved on adding ether, and, after scratching with a glass rod, separated as a powder.

Action of Concentrated Hydrochloric Acid on the Benzyl Ester of Carbethoxyhydroxamic Acid.

It is decomposed by this reagent slowly in the cold, more readily on warming, and α-benzylhydroxylamine hydrochloride is deposited in pearly scales, which sublime above 220°. When treated with potassium cyanate, delicate needles of the urea derivative, $OC\begin{matrix}NHOC_7H_7\\ \diagup\\ \diagdown\\ NH_2\end{matrix}$, melting at 138°, were obtained.

The neutral oil, formed as a bye-product in the above experiment, boiled at 190°–215° at 15 mm.; it has not been investigated.

The Action of Benzoyl Chloride on Salts of Carbethoxyhydroxamic Acid.

Benzoyl Ester of Carbethoxyhydroxamic Acid, $C_2H_5O—C\begin{matrix}O\\ \diagup\!\!\diagup\\ \diagdown\\ NHOCO.C_6H_5\end{matrix}$.—7.9 grams of carbethoxyhydroxamic acid were dissolved in water, and neutralized with 4.2 grams of potassium hydroxide. To this solution 10.1 grams (1 mol.) of benzoyl chloride were added. The mixture was shaken until the odor of benzoyl chloride became faint, and a colorless oil had separated. Without removing the oil, the contents of the flask were transferred to a separatory funnel, and extracted with ether. The benzoyl derivative was then extracted from the ether by means of dilute sodium hydroxide, and precipitated from this alkaline solution by means of carbon dioxide. A colorless oil separated, which was again taken up by ether. After drying and evaporating the ether, 8 grams of oil were obtained. After standing for

six months in a desiccator, this oil gave indications of solidifying, and in a few hours became a mass of soft, fibrous crystals, melting at 38°–39°.

0.3104 gram gave 18.6 cc. N_2 at 15° and 744.1 mm.

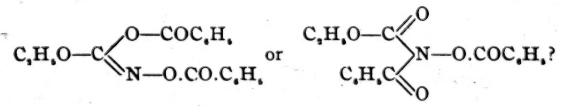
	Theory for $C_{10}H_{11}NO_4$.	Found.
N	6.69	6.89

Properties.—It can be distilled at diminished pressure, but suffers considerable decomposition; at 180°–190° and 20 mm., a colorless oil passes over, possessing an intense odor of isocyanates, and depositing crystals of benzoic acid on standing. This distillate can be dissolved in alkalies, and reprecipitated by carbon dioxide.

The solid is readily soluble in ether, alcohol, and ligroïn, almost insoluble in water. Alkalies decompose it, even in the cold, on standing for a short time, into benzoic acid, and carbethoxyhydroxamic acid.

Sodium Salt.—By the addition of sodium ethylate to an alcoholic solution of the acid, and precipitation with ether, a white salt is formed. A yellow silver salt separates on adding silver nitrate to a water solution of the sodium salt.

Dibenzoyl Derivative of Carbethoxyhydroxamic Acid,



1.5 grams of the sodium salt of the benzoyl ester of carbethoxyhydroxamic acid were suspended in absolute ether, and treated with 0.9 gram of benzoyl chloride; 1.9 grams of oil were obtained on evaporating the ether solution. This solidified partially to a mass of colorless crystals. Recrystallized from ether and ligroïn, it was obtained in transparent, prismatic crystals, melting at 72°–73°.

0.0965 gram gave 0.2301 gram CO_2, and 0.0426 gram H_2O.

0.3275 gram gave 13.4 cc. N_2 at 22° and 743 mm.

	Theory for $C_{17}H_{18}NO_4$.	Found.
C	65.17	65.03
H	4.79	4.90
N	4.47	4.55

Properties.—It is slightly soluble in warm ligroïn, readily soluble in ether, and alcohol.

Contributions from the Chemical Laboratories of the Massachusetts Institute of Technology.

XVIII.—THE ACTION OF THE HALOGENS ON THE ALIPHATIC AMINES, AND THE PREPARATION OF THEIR PERHALIDES.

By James F. Norris.

In a preliminary communication on the action of the halogens on the methylamines, Remsen and Norris[1] described the preparation and properties of some new compounds formed by the action of iodine on trimethylamine and of bromine on trimethyl- and dimethylamine. The discovery of the compounds was made in an investigation of some double salts containing selenium and the methylamines, and as their complete study was impossible at that time, a preliminary notice of the results was published. It was shown that a compound of the probable structure $(CH_3)_3N.I_3$ was formed when a solution of iodine in absolute alcohol was treated with dry trimethylamine. The addition-product was precipitated as a light yellow powder, insoluble in water, which rapidly darkened and changed to a viscous liquid after standing a few days. It was decomposed slowly by hot water, and gave up all its iodine when treated with dilute hydrochloric acid, forming trimethylamine hydrochloride according to the following equation;

$$(CH_3)_3N.I_3 + HCl = (CH_3)_3N.HCl + 2I.$$

By the action of bromine on dimethyl- and trimethylamine, compounds were formed, which crystallize from a mixture of alcohol and ether in yellow needles. Two possible formulas were considered, $(CH_3)_3N.HBr.Br$ and $(CH_3)_3N.Br_2$. As the trimethylamine compound was prepared at 0° from dry tri-

[1] This Journal, 18, 90.

methylamine and bromine which had been freed from hydrobromic acid and water by successive distillation from precipitated manganese dioxide and sulphuric acid, it was concluded that the second formula represented the structure of the compound. The formation of hydrobromic acid by the action of bromine on a methyl group at 0° seemed highly improbable. Further, all the perhalides described up to that time contained two or more added halogen atoms, for example, NH_4I_3, $CsBrI_2$, $CsBr_3$, and $C_5H_5N_5.IBr_2$. The action of bromine was accordingly considered analogous to that of iodine.

These compounds have now been carefully studied, and it has been found that the reactions of the bromides with a number of reagents are not analogous to those of the iodide. It follows, therefore, that they have different structures.

All the reactions of the iodide are in accord with the formula already proposed, $(CH_3)_3N.I_2$. Water does not liberate iodine; dilute acids set free all of the iodine and form the salt of the amine; and concentrated sulphuric acid does not cause an evolution of hydriodic acid, which would be the case if the formula were $(CH_3)_3N.HI.I$. A true periodide, $(CH_3)_3N.HI.I_2$, was treated with concentrated sulphuric acid. Hydriodic acid was set free, thus showing the value of the above test.

The bromide derived from trimethylamine, however, was decomposed by water with liberation of one-half of the bromine. The presence of dilute acids did not affect the decomposition, and concentrated sulphuric acid caused a vigorous evolution of hydrobromic acid. The most probable structure is, therefore, $(CH_3)_3N.HBr.Br$. The correctness of this view was further demonstrated by making the compound from trimethylamine hydrobromide and bromine. Direct addition took place without the formation of hydrobromic acid, thus showing that the hydrogen was not replaced by bromine. If the above structure is correct, bromine readily attacks a methyl group joined to nitrogen, forming hydrobromic acid, for the compound was prepared from pure bromine and pure trimethylamine at 0°. This was shown to be the case by the

following experiments: A cold ethereal solution of bromine, free from hydrobromic acid, was poured into a cold ethereal solution of trimethylamine. As long as the amine was in excess a white precipitate, which proved to be trimethylamine hydrobromide, was formed. On addition of an excess of bromine, the salt changed to a red oil, which proved, on crystallization, to be the bromine addition-product. It follows from this experiment that the hydrobromide is first formed, and from this the dibromide. In a second experiment the dry amine was passed into bromine, kept cool by ice, and the evolved gases passed into water. After the removal of free bromine with precipitated silver from the latter, hydrobromic acid was found. A blank experiment was performed by drawing air through the apparatus in order to test the value of the method. It is, therefore, evident that bromine is readily substituted for hydrogen in a methyl group joined to nitrogen. It has been impossible thus far to isolate the substitution-product formed. The only compound obtained was the perbromide. Pyridine perbromides and periodides of a similar structure have been recently described by Trowbridge and Diehl.[1]

The action of iodine and bromine on a number of aliphatic amines has been studied in order to determine whether the formation of iodine addition-products and perbromides is general. Trimethylamine is the only amine studied which gives a diiodo addition-product. Dimethylamine reacted with iodine dissolved in ether and gave a compound containing two iodine atoms, but its reaction showed that its formula is $(CH_3)_2HN.HI.I$, analogous to the bromides. Diamylamine gave the periodide $(C_5H_{11})_2NH.HI.I_2$. The action of iodine on the amines and their salts is being further investigated.

The reaction between bromine and tricetylamine was studied in order to discover whether the power to form perbromides exists with compounds containing a large number of carbon atoms. No reaction took place. Perbromides were formed from dimethyl, trimethyl, diethyl, triethyl, dipropyl, tripropyl and diamylamines. As the number of carbon atoms increased

[1] J. Am. Chem. Soc., 19, 558.

the stability of the compounds and their crystallizing power decreased. The propyl and amyl compounds are red oils which crystallize with difficulty and decompose on standing. They all have the structure $R_3N.HBr.Br$, where one R may be hydrogen, and all give off one atom of bromine when dissolved in water. No perbromides of primary amines could be isolated.

By the action of chlorine on trimethylamine a very unstable compound, having the appearance and odor of camphor, was formed. It was impossible to purify or analyze it.

The following perhalides of dimethylamine containing two different halogens have been prepared: $(CH_3)_2NH.HCl.Br$, $(CH_3)_2NH.HCl.I$, $(CH_3)_2NH.HBr.I$. The salts containing two bromine and two iodine atoms are well characterized as stated above, but a number of methods failed to produce the compound containing two chlorine atoms. Analogous compounds containing trimethylamine were prepared. The ease of formation of these perhalides containing two halogens is in accord with the observation of Wheeler[1] that organic compounds form such salts with greater facility than the alkali metals.

Pictet and Krafft[2] have described the compound $(CH_3)_3N.ICl$. Efforts were made to repeat the work as described, but without success. The compound always obtained was the diiodide $(CH_3)_3N.I_2$. By the action of iodine monochloride on trimethylamine the salt $(CH_3)_3N.HCl.I$ was obtained.

Incidentally an improved modification of the method for the preparation of dimethyl- and diethylamine from dimethyl- and diethylaniline is described.

Experimental Part.

WITH E. H. LAWS.

Preparation of Dimethylamine. — A modification of the method of Baeyer and Caro[3] was used, which shortened the process and gave excellent results. 100 grams of nitrosodimethylaniline hydrochloride, prepared as directed by Levy

[1] This JOURNAL, 19, 672. [2] Bull. Soc. Chim. (Paris), [3], 7, 74.
[3] Ber. d. chem. Ges., 7, 964.

(Anleitung zur Darstellung organischer Präparate), was rubbed into a thin paste with warm water and introduced slowly through a funnel with a wide neck into a four-liter flask, provided with a return-condenser, and containing a boiling solution of 90 grams sodium hydroxide dissolved in two liters of water. A glass rod covered with rubber tubing was used as a stopper to close the funnel during the decomposition. The evolved gas was absorbed in hydrochloric acid (sp. gr. 1.12) contained in two Peligot tubes. Almost the theoretical amount of nitrosodimethylaniline hydrochloride is obtained and about a 90 per cent. yield of dimethylamine hydrochloride. About ten hours were required to set up the apparatus and prepare 200 grams of the hydrochloride by this method.

Dimethylammonium Dibromide, $(CH_3)_2NH.HBr.Br$.—The best method of preparation is as follows: 10 grams of dimethylamine hydrobromide are cautiously treated with 8 grams of bromine. After the cooled solid mass is dried on a porous plate over potassium hydroxide, it is dissolved in cold alcohol, and ether is added until precipitation begins. The solution is cooled with a freezing-mixture when the compound crystallizes in yellow needles. Addition of more ether causes a further precipitation. The salt is very soluble in alcohol, sparingly soluble in hot chloroform and insoluble in ether. It melts at 93° and does not decompose when heated to 200°. When treated with water it melts, forming a heavy red oil, which slowly dissolves. One-half of the bromine is set free, as was shown in a former paper. As the total iodine in the diiodide of trimethylamine was liberated by dilute hydrochloric acid, the amount of halogen set free from the bromide under the same conditions was determined.

0.1498 gram salt gave 0.0587 gram bromine.

Calculated for 1Br.	Found.
38.88	39.23

It is seen, therefore, that the structure of the bromide is not $(CH_3)_2NH.Br_2$. A complete analysis gave the following results:

I. 0.5240 gram salt gave 0.2307 gram CO_2, and 0.1860 gram H_2O.

II. 0.3981 gram salt gave 0.1705 gram CO_2, and 0.1430 gram H_2O.

III. 0.1628 gram salt gave 0.2967 gram AgBr by the Carius method.

IV. 0.4987 gram salt gave 27.7 cc. nitrogen at 0° and 760 mm.

	Calculated for $(CH_3)_2NH.HBr.Br$.	Found. I.	II.	III.	IV.
C	11.65	12.00	11.69	....	....
H	3.88	3.98	4.02	....	....
N	6.79	....	....	....	6.77
Br	77.67	....	....	77.56	....

The perbromide was treated with a large excess of bromine in an attempt to prepare a salt containing more halogen atoms. When the excess of bromine was removed by slow evaporation the original salt was obtained. Dry chlorine was passed over a weighed quantity of the perbromide. The loss in weight and analysis of the resulting product showed that but one-half of the bromine was removed, and the formula of the resulting substance was $(CH_3)_2NH.HCl.Br$.

Dimethylammonium Triiodide, $(CH_3)_2NH.HI.I_2$.—An attempt was made to prepare the dimethylammonium diiodide in a manner similar to that used with the dibromide. Dimethylamine hydroiodide in hydriodic acid was treated with iodine. The salt obtained was purified by dissolving in a small amount of ethyl acetate and adding benzene, when it crystallized in long needles with a dark-blue, steely luster. Analysis showed that it was a triiodide.

I. 0.2038 gram salt gave 0.3374 gram AgI.

II. 0.2912 gram salt gave 0.1733 gram free iodine when treated with water.

	Calculated for $(CH_3)_2NH.HI.I_2$.	Found. I.	II.
3I	89.20	89.45	....
2I	59.47	....	59.53

The formation of a periodide of dimethylamine has been noted by Schmidt,[1] but no formula is assigned to it. The triiodide melts at 97°, is soluble in alcohol and ether, insoluble

[1] Ann. Chem. (Liebig), **267**, 254.

in chloroform and carbon disulphide. Water decomposes it into the hydroiodide and free iodine, and potassium hydroxide forms iododimethylamine $(CH_3)_2NI$.

Dimethylammonium Diiodide, $(CH_3)_2NH.HI.I$.—The direct addition-product of trimethylamine and iodine is precipitated when the constituents are mixed in alcoholic solution. No precipitate was formed, however, when dimethylamine was used. Evaporation of the solution did not yield a pure product. As the diiodide could not be prepared in this way, an excess of the dry amine was passed into an ethereal solution of iodine. A dark oil separated, which was analyzed after the removal of the ether on a water-bath.

I. 0.3354 gram salt gave 0.5247 gram AgI.

II. 0.3576 gram salt gave 0.5570 gram AgI.

Calculated for $(CH_3)_2NH.HI.I$.	Found.	
	I.	II.
84.65	84.53	84.16

The salt formed was not analogous to the trimethylamine compound, for but one-half of the iodine was liberated in acid solution and hydriodic acid was evolved with concentrated sulphuric acid. It accordingly has the structure $(CH_3)_2NH.HI.I$, similar to that of the bromides.

Dimethylammonium Chloriodides. — Dimethylammonium chloriodide, $(CH_3)_2HN.HCl.I$, was prepared by treating dimethylamine hydrochloride, dissolved in alcohol and chloroform, with iodine, using the constituents in the proportion of one molecule of the former to one atom of the latter. It crystallized slowly in dark-red needles. The substance was analyzed by reducing the iodine set free with sulphur dioxide, and precipitating with silver nitrate. The mixture of silver halides was weighed, then treated with chlorine and weighed again. The results follow:

I. 0.2428 gram salt gave 0.4431 gram AgI + AgCl, which lost 0.1070 gram.

II. 0.2770 gram salt gave 0.5036 gram AgI + AgCl, which lost 0.1212 gram.

III. 0.1502 gram salt gave 0.0926 gram free I.

	Calculated for $(CH_3)_2HN.HCl.I$.	Found. I.	II.	III.
Cl	17.01	17.13	17.17	....
I	60.88	61.16	60.72	61.67

The salt melts at 100° and dissolves in water with liberation of all of the iodine. Potassium hydroxide forms iododimethylamine.

When a weighed quantity of this chloriodide was treated with dry chlorine, it melted and the gas was absorbed. After a few hours, during which the salt was gently heated, the increase in weight was equivalent to a molecular quantity of chlorine. The resulting product crystallized from a mixture of alcohol and ether in yellow needles, and gave results on analysis closely approximating the formula $(CH_3)_2NH.HCl.ICl_2$.

Dimethylammonium Chlorbromide, $(CH_3)_2NH.HCl.Br$. — This salt was prepared by the action of bromine on dimethylamine hydrochloride, dissolved in hydrochloric acid, or in chloroform. Addition of carbon disulphide to the chloroform solution causes a precipitation of the compound. It is also formed by the action of chlorine on the perbromide, $(CH_3)_2NH.HBr.Br$. The analysis resulted as follows:

0.3021 gram salt gave 0.6004 gram AgCl + AgBr, which lost 0.0778 gram when treated with chlorine.

	Calculated for $(CH_3)_2NH.HCl.Br$.	Found.
Cl	21.93	22.22
Br	49.55	46.26

Dimethylammonium Bromiodide, $(CH_3)_2NH.HBr.I$.—This compound was prepared from the bromide and iodine in a manner similar to that used to make the chlorbromide. It is a dark-red, crystalline salt, which melts at 98°–99°.

WITH F. M. SMALLEY.

The work described in this section was done before the correct structure of the substances formed by the action of the halogens on the amines was made clear. Efforts were made to prepare compounds similar to the diiodide of trimethylamine, $(CH_3)_3N.I_2$, by the action of iodine chloride, bromine chloride, and iodine bromide on the free amine. These com-

pounds, however, act like bromine, causing substitution, and forming perhalides. It was found later that the latter could be prepared more advantageously by the method described above for the dimethylamine salts.

Trimethylammonium Chloriodides.—The salt containing two halogen atoms was prepared as follows: A solution of trimethylamine in alcohol was treated with a chloroform solution of iodine monochloride. After standing a few hours in a vacuum-desiccator, the compound crystallized in dark reddish-brown needles, which melt at 84°. With water, iodine was set free. The following analyses were made:

I. 0.1370 gram salt gave 0.2305 gram AgI + AgCl, which gave 0.1753 gram AgCl.

II. 0.1619 gram salt gave 0.2723 gram AgI + AgCl, which gave 0.2064 gram AgCl.

	Calculated for $(CH_3)_3N.HCl.I.$	Found. I.	II.
I	57.05	55.91	56.49
Cl	16.00	16.02	15.76

By the action of iodine trichloride on the amine, a second perchloride was obtained. When the substances were mixed in alcoholic solution the temperature rose and a yellow precipitate separated. Before this could be filtered off it dissolved, forming a dark red solution, from which reddish-brown crystals separated on standing, which melted at 84°, and on analysis proved to be the chloriodide, $(CH_3)_3N.HCl.I$. The preparation was repeated, care being taken to keep the solution cold. The yellow precipitate was removed and dried on a porous plate. It melted at 168°, and on treatment with water it decomposed, liberating chlorine and iodine. The analysis was made as follows: The salt was dissolved in dilute sulphurous acid, the excess of which was removed by gentle heating. An excess of standardized silver nitrate was added; the precipitate filtered off, dried and weighed. The excess of the silver nitrate in the filtrate was titrated with ammonium sulphocyanate. The method gives much better results than the treatment of the mixed silver halides with chlorine or bromine and requires less time. The results follow:

I. 0.3671 gram salt gave 0.8242 gram AgCl + AgI, and required 0.5345 gram Ag for precipitation.

II. 0.3909 gram salt gave 0.8826 gram AgCl + AgI, and required 0.5735 gram Ag for precipitation.

	Calculated for $(CH_3)_3N.HCl.ICl_2$.	Found. I.	II.
Cl	36.40	35.87	36.27
I	43.40	42.95	42.80

Trimethylammonium Chlorbromide, $(CH_3)_3N.HCl.Br$.—This compound was prepared by the action of chlorine on the dibromide, and of bromine on the hydrochloride dissolved in hydrochloric acid. It crystallizes in yellow needles and dissolves in water with evolution of bromine. The analysis gave figures approximating the above formula.

Trimethylammonium Bromiodide, $(CH_3)_3N.HBr.I$.—To a chloroform solution of iodine bromide was added an alcoholic solution of trimethylamine. After standing in a vacuum-desiccator for a number of days a mixture of white and red crystals appeared. The former proved to be the trimethylamine hydrobromide, and the latter the bromiodide. This salt crystallizes in maroon needles, melts at 89°, and gives up iodine when acted upon by water. The analyses follow :

I. 0.4501 gram salt gave 0.7113 gram AgI + AgBr, and required 0.3624 gram Ag for precipitation.

II. 0.4557 gram salt gave 0.7338 gram AgI + AgBr, and required 0.3745 gram Ag for precipitation.

	Calculated for $(CH_3)_3N.HBr.I$.	Found. I.	II.
Br	30.00	29.35	28.97
I	47.50	48.11	48.50

Action of Chlorine on Trimethylamine.—Dry chlorine and dry trimethylamine react, forming a very hygroscopic substance, which evolves chlorine in the air. The two gases were passed into absolute ether, which was well cooled. A heavy white precipitate formed, which decomposed spontaneously when the ether was removed. It was impossible to determine the composition of the substance.

WITH A. E. KIMBERLY.

Preparation of Diethylamine.—The method of Kopp[1] for

[1] Ber. d. chem. Ges., 8, 621.

the preparation of diethylamine was much shortened by proceeding as follows: A solution of 50 grams of diethylaniline in 148 grams of hydrochloric acid (sp. gr. 1.12) diluted with 75 cc. water, was diazotized with 32 grams of sodium nitrite, dissolved in 50 cc. of water. The nitrite was added to the solution cooled by ice and salt. After standing a few minutes the solution of nitrosodiethylaniline hydrochloride was slowly run into a four-liter flask provided with a condenser, and containing a boiling solution of 85 grams of sodium hydroxide dissolved in two liters of water. The solution of diethylamine which distilled over was collected in dilute hydrochloric acid. The contents of the flask were boiled for three-quarters of an hour after all the nitroso compound had been introduced. A yield of 75 per cent. of diethylamine was obtained after rectification.

Diethylammonium Dibromide, $(C_2H_5)_2NH.HBr.Br.$[1]—This salt was prepared by adding an ethereal solution of the amine to an ethereal solution of bromine. Also by the action of bromine on the hydrobromide. It crystallizes in reddish-yellow needles, and when treated with potassium hydroxide yielded a heavy yellow, insoluble oil, which is being further investigated. The following analysis was made:

0.2071 gram salt gave 0.3220 gram AgBr.

	Calculated for $(C_2H_5)_2NH.HBr.Br.$	Found.
Br	68.33	68.22

Experiments with Triethylamine. — Triethylamine was treated with bromine, both in ethereal solution. When there was an excess of the amine the hydrobromide was formed. An excess of bromine caused the separation of an oil which did not solidify after standing three weeks. It could not be purified from the excess of bromine without decomposition. The hydrobromide of the amine was treated with bromine in the way used in the preparation of the perbromide of dimethylamine. A red oil resulted, which could not be purified. Evidently the perbromide, if formed, was very unstable.

[1] This salt, as well as the dibromide from diamylamine was prepared and analyzed by L. L. Lamborn.

Dipropylammonium Dibromide, $(C_3H_7)_2NH.HBr.Br.$—This compound was prepared in the usual way from the hydrobromide and bromine. The resulting oil on long standing crystallized. It was purified by dissolving in alcohol and adding ether. Reddish-yellow crystals separated when the solution was cooled by ice and salt. In properties it resembles the other perbromides, but is much less stable, as shown by the analysis. The sample used had no odor of bromine.

0.1995 gram salt gave 0.2507 gram AgBr.

	Calculated for $(C_3H_7)_2.NH.HBr.Br.$	Found.
Br	61.01	55.21

When treated with sodium hydroxide the perbromide gives a yellow oil with a strong odor.

Tripropylammonium Dibromide, $(C_3H_7)_3N.HBr.Br.$ — The method used in the preparation of the dipropyl compound was followed here. The body readily loses bromine. Analysis of crystals washed free from bromine with petroleum ether gave the following results:

0.2138 gram salt gave 0.2600 gram AgBr.

	Calculated for $(C_3H_7)_3N.HBr.Br.$	Found.
Br	54.98	52.00

Diamylammonium Dibromide, $(C_5H_{11})_2NH.HBr.Br.$ — Diamylamine and bromine in ethereal solution gave a red oil, which after washing with ether was analyzed.

0.3061 gram salt gave 0.3536 gram AgBr.

	Calculated for $(C_5H_{11})_2NH.HBr.Br.$	Found.
Br	50.31	49.18

Experiments with Tricetylamine.—Tricetylamine, prepared according to Fridau's[1] directions, was dissolved in ether and treated with bromine. As no precipitate was formed the ether was evaporated, when a dark oil appeared, which solidified to a white mass after it was washed free from bromine. After drying, it melted at 38°–40° and contained no bromine. Tricetylamine melts at 39°. It is evident, therefore,

[1] Ann. Chem. (Liebig), 83, 25.

that the power to form perbromides exists only with the amines containing a small number of carbon atoms.

Investigation of the Structure of the Compounds.—Trimethylamine diiodide, $(CH_3)_3N.I_2$, was prepared according to the directions already given. It was treated with dilute hydrochloric acid, and the iodine set free titrated with sodium thiosulphate. All of the iodine in the compound was liberated. Another portion was treated with concentrated sulphuric acid. There was a separation of iodine, but no hydriodic acid was formed, whereas the gas was easily recognized when a perhalide, $(CH_3)_3N.HI.I_2$, was acted on by sulphuric acid.

The dibromide was studied in the same way. Dilute hydrochloric acid did not affect the decomposition with water, which liberated one-half of the bromine, and concentrated sulphuric acid caused a vigorous evolution of hydrobromic acid. Three grams of trimethylamine hydrobromide were treated in a dry flask with pure bromine. Air was drawn through the flask and then through water. When the reaction was complete the latter was shaken with precipitated silver, filtered, and titrated with tenth-normal sodium hydroxide. 0.3 cc. of the alkali was used, thus showing that no hydrobromic acid was evolved, and that the compound was formed by the direct addition of bromine to the hydrobromide.

The salt was also prepared by the action of pure bromine on pure trimethylamine, both dissolved in ether, and in absence of a solvent. The formula $(CH_3)_3N.HBr.Br$ requires hydrobromic acid. The following experiment showed that the hydrogen necessary was furnished by the amine. To a cold solution of trimethylamine in ether, was added a cold solution of pure bromine in ether. As long as the amine was in excess a white precipitate was formed. This on analysis proved to be trimethylamine hydrobromide. The other product of reaction could not be isolated. Carefully dried trimethylamine was passed into bromine cooled by ice-water. The evolved gas was drawn through water which, after the removal of free bromine, was titrated with a standard alkali. A blank determination was made by drawing air through the apparatus. In both cases the experiment was continued for

an hour. Acid equivalent to 1.5 cc. tenth-normal sodium hydroxide was obtained with the blank, whereas 14 cc. were required for neutralization when the amine was used. It follows that more hydrobromic acid than is necessary to unite with all the amine is formed by the direct action of bromine.

Attempts to Prepare the Compound $(CH_3)_3N.ICl$.—Pictet and Krafft[1] have described a compound of the above formula which is analogous to the diiodide prepared by us, $(CH_3)_3N.I_2$. As the chloriodine addition-product was not obtained by the direct action of iodine monochloride on trimethylamine, efforts were made to obtain it according to Pictet and Krafft. The directions given were followed, but without success. By the action of iodine trichloride on trimethylamine, they obtained a compound of the formula $(CH_3)_3N.HCl.ICl$, which crystallized in yellow leaflets and melted at 159°. When this was treated with sodium carbonate the addition-product $(CH_3)_3N.ICl$ was formed as a precipitate, which crystallized from ether. The yellow salt was formed as described, but treatment of a solution of it with sodium carbonate, under a variety of conditions, yielded only the diiodide, $(CH_3)_3N.I_2$.

BOSTON, MASS., November 1, 1897.

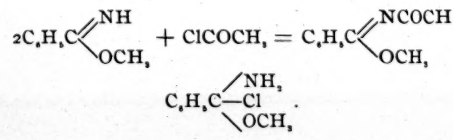
Contributions from the Sheffield Laboratory of Yale University.

LV.—ON ACYL IMIDO ESTERS.

SECOND PAPER.

BY H. L. WHEELER, P. T. WALDEN, AND H. F. METCALF.

In a previous paper, by two of us, it was shown that the imidomethyl and ethyl benzoates give acyl derivatives with acetyl and benzoyl chloride, the reaction taking place as follows:



Two molecules of the imido ester react with one molecule of

[1] Bull. Soc. Chim. [Paris], [3], 7, 74.

acyl chloride, giving one molecule of acylimido ester and one molecule of the imido ester hydrochloride.

We now find that the acylimido esters may also be prepared from the silver salts of diacyl amides. Silver dibenzamide gave, with ethyl iodide, a product identical in every respect with that obtained from benzimidoethyl ester and benzoyl chloride; *i. e.*, $C_6H_5C\begin{matrix}=NCOC_6H_5\\ -OC_2H_5\end{matrix}$. The product had entirely different properties from those of the isomeric nitrogen ethyl compound, $C_6H_5CON(C_2H_5)COC_6H_5$, which was prepared from ethylbenzamide. The reaction, therefore, takes place as follows:

$$C_6H_5C\begin{matrix}=NCOC_6H_5\\ -OAg\end{matrix} + IC_2H_5 = C_6H_5C\begin{matrix}=NCOC_6H_5\\ -OC_2H_5\end{matrix} + AgI.$$

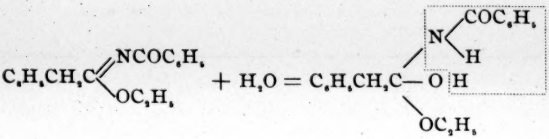
The behavior of the silver salts of diacyl amides towards ethyl iodide is thus shown to be perfectly analogous to that of the silver salts of monoacylamides[1] and anilides.[2]

The acylimido esters are very reactive substances, and it was with difficulty that some were obtained in a state of approximate purity. They react with water, immediately in the presence of acids, in either of two ways; *i. e.*, alcohol is separated, and a diacylamide results, or a monoacylamide and an ester are formed. These decompositions may be represented as follows:

$$C_6H_5C\begin{matrix}=NCOC_6H_5\\ -OCH_3\end{matrix} + H_2O = C_6H_5C\begin{matrix}=N-COC_6H_5\\ -OH\\ -OCH_3\end{matrix}$$

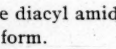
As far as observed, the acetyl, propionyl, butyryl, carbethoxyl, and benzoylbenzimido esters behave in the above manner, while benzoylphenylacetimidoethyl ester and those imido esters containing the acyl group, —COCO.OC_2H_5, do not give diacyl amides, but readily decompose as follows:

[1] Tafel and Enoch: Ber. d. chem. Ges., **23**, 104.
[2] Comstock and Kleeburg: *Ibid*, **12**, 493.

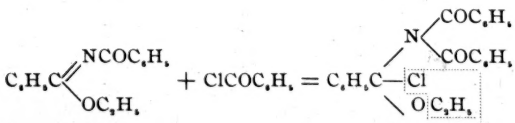


These reactions show conclusively that the diacyl amides have both acyl groups attached to nitrogen.

To what extent the acylimido esters decompose according to the first representation, otherwise than indicated above, remains to be investigated. At present this decomposition suggests an easy method for the preparation of certain diacyl amides, it being only necessary to treat the reaction-product of an acyl chloride and an imido ester, with hydrochloric acid, when the diacyl amide immediately separates pure and in crystalline form.

The instability of the acylimido esters in the presence of moisture, acids, etc., recalls the similar behavior of the oxygen ethers of succinimide,[1] which readily separate alcohol and revert to succinimide. The grouping  becomes less stable in the presence of moisture as the negative character of the groups R and R′ are increased.

When benzoylbenzimidoethyl ester is heated with benzoyl chloride it reacts slowly and tribenzamide results:

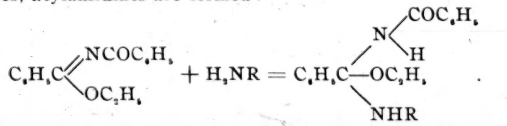


This reaction is analogous to the action of acyl chlorides on the isoanilides,[2] in which case diacylanilides were formed. It therefore indicates that in the triacylamides all three acyl groups are attached to nitrogen. An attempt was made to determine the structure of the triacylamides and to prove the

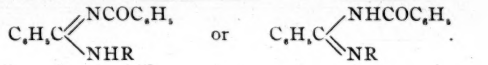
[1] Comstock and Wheeler: This JOURNAL, **13**, 519.
[2] Wheeler and Walden: This JOURNAL, **19**, 129.

equivalence of the three bonds of nitrogen, in respect to acyl groups, by allowing benzoyl chloride to react on acetylbenzimidoethyl ester, on the one hand, and acetyl chloride on benzoylbenzimidopropyl ester on the other. Tribenzamide, however, was formed in the first case while, in the second, nothing but decomposition-products were observed.

When the acylimido esters are treated with ammonia or bases, acylamidines are formed:

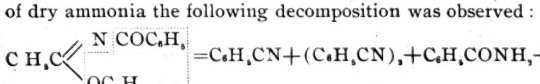


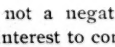
The structure of these cannot be determined by their method of formation since the above hypothetical addition-product can give up alcohol in two ways, giving either



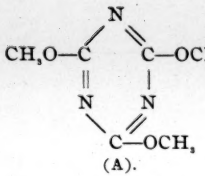
The acylamidines will be described in a later paper.

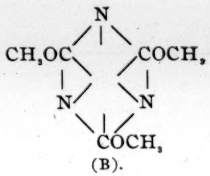
When benzoylbenzimidoethyl ester was heated in a stream of dry ammonia the following decomposition was observed:



The violence with which acyl chlorides, but especially acetyl chloride, react with the imido esters, isoanilides, or compounds containing the arrangement  , in which the radical R' is not a negative (acyl) group, suggests that it would be of interest to compare the behavior of some rings supposed to contain this grouping. At present we have tried the trimethyl ester of normal cyanuric acid. This, if constituted as described in the text-books, formula (A), contains three of the above groups and should react, giving the triacetyltricarbonimide of Ponomarew.[1]

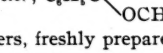
[1] Ber. d. chem. Ges., 18, 3275.


(A).


(B).

The trimethyl ester was prepared by the directions of Hofmann[1] from cyanuric chloride and sodium methylate. It was then found that this ester can be crystallized unaltered from acetyl chloride, and no action at the boiling-point of acetyl chloride was observed. It seems, therefore, improbable that there are three double unions in the normal cyanuric esters, or, which is practically the same, that they contain para bonds. The inertness of this ester, however, might be explained by the centric formula (B), or it may be due to the ring formation. It is our intention to continue this work on the action of acyl chlorides on ring-formed compounds which, theoretically, may be considered as derived from the grouping .

Experimental Part.

Benzimidomethyl Ester,  .—For the preparation of acylimido esters, freshly prepared and distilled imido esters were used. The imido ester hydrochlorides were prepared by Pinner's well-known method, and the free esters according to Bushong's directions.[2]

This compound boiled at 96° under a pressure of 13 mm. Bushong found it to boil at 96° at 10 mm. In a previous paper[3] it was stated that benzimidomethyl ester deposits benzamide on standing. This is not the case when the ester is prepared from benzonitrile by the method of Pinner, and then distilled. The pure ester may be kept for months without

[1] Ber. d. chem. Ges., **19**, 2063. [2] This JOURNAL, **18**, 490.
[3] This JOURNAL, **17**, 398.

any apparent change. A specimen exposed in a test-tube plugged with cotton, after standing a year, deposited a few crystals. These melted at 230°, and were, therefore, cyanphenine.

The Picrate, $C_6H_5C\begin{matrix}NH\\ \diagdown\\ OCH_3\end{matrix}.C_6H_2(NO_2)_3OH$.—An alcoholic solution of picric acid added to benzimidomethyl ester in ether gives a heavy, lemon-yellow, crystalline precipitate. This melts at 163° and from alcohol or water it forms stout prisms. A nitrogen determination gave:

	Calculated for $C_{14}H_{12}N_4O_8$.	Found.
N	15.38	15.06

Benzoylbenzimidomethyl Ester, $C_6H_5C\begin{matrix}NCOC_6H_5\\ \diagdown\\ OCH_3\end{matrix}$. — When benzoyl chloride is mixed with benzimidomethyl ester in ethereal solution, in the proportion of one molecule of the former to two of the latter the reaction is practically complete in twenty-four hours. It was found advisable to treat the reaction-product here, as in most of the other cases, as follows: On filtering from the imido ester hydrochloride, the ether solution was shaken with dilute alkali, dried over solid potassium hydrate, then calcium chloride, and finally, on evaporating off the ether, the products were usually obtained as oils. This compound, unlike the corresponding ethyl and isobutyl derivatives, refused to solidify without decomposition. It was found to boil from 210° to 212° at 12 mm. pressure. A nitrogen determination in the colorless oil thus obtained gave:

	Calculated for $C_{15}H_{13}NO_2$.	Found.
N	5.8	5.5

When benzoylbenzimidomethyl ester is treated with a drop of hydrochloric acid in alcoholic solution, dibenzamide separates. Dibenzamide is also deposited when the material is allowed to stand.

Carbethoxylbenzimidomethyl Ester, $C_6H_5C\begin{matrix}NCO_2C_2H_5\\ \diagdown\\ OCH_3\end{matrix}$. —

Benzimidomethyl ester and chlorcarbonic ethyl ester were boiled in ethereal solution for a number of hours. On cooling the ethereal solution, plates separated. These melted at about 126° and on crystallizing from water melted at 128°. This material proved to be benzamide. The ether was evaporated, and a mixture of oil and crystals of benzamide obtained; on distilling this at 14 mm. it was found to boil from 148° to 156°. This fraction was treated with a mixture of equal volumes of ether and ligroïn, filtered from precipitated benzamide, and then, after evaporating the solvent, a colorless oil was obtained which boiled at 155° at 14 mm. pressure. A nitrogen determination gave the following result:

	Calculated for $C_{11}H_{13}NO_3$.	Found.
N	6.7	6.9

Benzoylurethane, $C_6H_5CONHCO_2C_2H_5$.—A few drops of the above material were treated with cold dilute hydrochloric acid, the mass then solidified and, on washing with water, it melted from 110°–111°. This solid dissolved readily in dilute sodium hydroxide, and was precipitated unaltered by dilute hydrochloric acid. It had all the properties of benzoylurethane, as described by Pechmann.[1]

Ethyloxalylbenzimidomethyl Ester, $C_6H_5C\begin{matrix}=NCOCO_2C_2H_5\\ \diagdown OCH_3\end{matrix}$.—7.7 grams of ethyl chloroxalate were slowly dropped into 15.4 grams of benzimidomethyl ester, largely diluted with dry ether. The reaction is violent and is complete when the ester is all added. On filtering and evaporating the ether a clear colorless oil was obtained. This was distilled at 23 mm. pressure. Below 206° a few drops collected, the latter portion of which solidified in flattened prisms, which melted at 114°–115° and proved to be oxamethane. From 206°–207° a thick syrup distilled over, which constituted almost the entire portion. It was redistilled at 14 mm., when it boiled at 192°. The latter portion of this distillate gave on analysis:

	Calculated for $C_{12}H_{13}NO_4$.	Found.
N	5.95	6.21

[1] Ber. d. chem. Ges., **28**, 2383.

When ethyloxalylbenzimidomethyl ester is exposed to the air for some time, or when boiled with water, the odor of benzoic ester is noticed and oxamethane results. The formation of benzoyloxamethane was not observed in this case, the decomposition taking place according to the second method mentioned in the introduction. Concentrated aqueous ammonia immediately decomposes this acylimido ester into oxamide and methyl benzoate. It soon solidifies when mixed with aniline.

Benzimidoethyl Ester, $C_6H_5C\begin{matrix}NH\\ \diagdown\\ OC_2H_5\end{matrix}$.—This was prepared by the method of Pinner. It was observed to distil at 101°–102° at 15 mm. pressure. Bushong[1] gives its boiling-point as 106°–109° at 15 mm.

Benzimidoethylester Mercuric Chloride, $C_6H_5C\begin{matrix}NH.HgCl\\ \diagdown\\ Cl\\ \diagdown\\ OC_2H_5\end{matrix}$.—Not only do the imido esters give well-crystallized addition-products with picric acid, but also in some cases with mercuric chloride. The above was prepared by adding benzimidoethyl ester to an alcoholic solution of mercuric chloride. The addition-product then separates in a mass of colorless needles. It was recrystallized from ether, and a chlorine determination gave the following result:

	Calculated for $C_9H_{11}NOHgCl_2$.	Found.
Cl	16.9	16.9

Acetylbenzimidoethyl Ester, $C_6H_5C\begin{matrix}NCOCH_3\\ \diagdown\\ OC_2H_5\end{matrix}$.—This compound we described in a previous paper. We have now prepared it in larger quantities, and find its boiling-point to be 156° at 17 mm. instead of 151°.

When acetylbenzimidoethyl ester is mixed with benzoyl chloride, and the mixture kept at a temperature of 100°–120° for a number of hours, a mass of needles separates. This proved to be tribenzamide.

[1] *Loc. cit.*

Propionylbenzimidoethyl Ester, $C_6H_5C\begin{matrix}=NCOC_2H_5\\ OC_2H_5\end{matrix}$.—The mixture in this case was allowed to stand for twenty-four hours, and then treated as in the case of benzoylbenzimidomethyl ester. The product was an oil which, on fractioning, boiled between 161° and 162° at 17 mm. pressure. A nitrogen determination gave:

	Calculated for $C_{12}H_{15}NO_2$.	Found.
N	6.83	7.08

Propionylbenzamide, $CH_3CH_2CO.NHCOC_6H_5$.—When the ethereal solution of propionylbenzimidoethyl ester is shaken with a few drops of concentrated hydrochloric acid, and the ether evaporated, this diacyl amide separates in the form of needles or prisms. Crystallized from alcohol it melts at 98°. A nitrogen determination gave:

	Calculated for $C_{10}H_{11}NO_2$.	Found.
N	7.91	8.08

Normal Butyrylbenzimidoethyl Ester, $C_6H_5C\begin{matrix}=NCOC_3H_7\\ OC_2H_5\end{matrix}$.—Normal butyryl chloride produces an immediate precipitate when added to benzimidoethyl ester dissolved in ether. The mixture was allowed to stand twenty-four hours, and then treated as in the case of benzoylbenzimidomethyl ester. The product was an oil which, on fractioning, boiled at 167° at 16 mm. pressure. A nitrogen determination gave:

	Calculated for $C_{13}H_{17}NO_2$.	Found.
N	6.39	6.64

Normal Butyrylbenzamide, $C_3H_7CO.NH.COC_6H_5$. — On shaking the ethereal solution of the above acylimido ester with concentrated hydrochloric acid, this compound separates in the form of beautiful colorless prisms. These, after three crystallizations from alcohol, melted constantly at 104°–105°. A nitrogen determination gave:

	Calculated for $C_{11}H_{13}NO_3$.	Found.
N	7·33	7·96

Benzoylbenzimidoethyl Ester, $C_6H_5C\begin{matrix}=NCOC_6H_5\\ \diagdown OC_2H_5\end{matrix}$.—This acyl-imido ester is the easiest to obtain in the solid condition, and therefore probably purer than the corresponding benzoylbenzimidomethyl and propyl esters, which were obtained only in the form of oils. In addition to the method already given, this compound was prepared from silver dibenzamide, as follows: 12 grams of the silver salt, dried at 100°, were suspended in ether and boiled with an excess of ethyl iodide. After several hours the ether, on evaporation, gave an oil, which soon solidified, giving the characteristic lozenge-shaped crystals melting at 65°. Sulphuric acid converted the material into dibenzamide.

Tribenzamide, $(C_6H_5CO)_3N$.—4.0 grams of the above compound were heated with 2.2 grams of benzoyl chloride. Little or no reaction took place below 100°, even at 130°–150° the evolution of gas (ethyl chloride) was slow. After several hours crystals were obtained. These, when crystallized from alcohol, melted at about 202°, and were, therefore, tribenzamide. A nitrogen determination gave:

	Calculated for $C_{21}H_{15}NO_3$.	Found.
N	4.25	4.39

Ethyldibenzamide, $(C_6H_5CO)_2NC_2H_5$.—For the preparation of this compound, which is isomeric with benzoylbenzimidoethyl ester, we wish to express our thanks to Mr. T. E. Smith. He prepared this amide as follows: Ethylbenzamide was prepared by the Baumann-Schotten method. The sodium salt of this, suspended in toluene with benzoic anhydride, gave ethyldibenzamide. The product thus obtained crystallized from alcohol in colorless prisms, melting at 101°–102°. A nitrogen determination gave:

	Calculated for $C_{16}H_{13}NO_2$.	Found.
N	4.9	5.2

Ethyloxalylbenzimidoethyl Ester, $C_6H_5C\begin{matrix}=NCOCO_2C_2H_5\\ \diagdown OC_2H_5\end{matrix}$.—

Ethyl chloroxalate reacts violently when mixed with benzimidoethyl ester dissolved in ether. The product is an oil which, on fractioning, boils from 190°–195° at 11 mm. pressure. The crude material generally contains oxamethane which distils over in the first portions. An analysis of the above fraction gave the following result :

	Calculated for $C_{13}H_{15}NO_4$.	Found.
N	5.8	6.0

This material readily decomposes into oxamethane and ethyl benzoate. The formation of benzoyloxamethane was not observed.

Benzimido(normal)propyl Ester, $C_6H_5C\begin{matrix}NH\\ \diagup\\ \diagdown\\ OCH_2CH_2CH_3\end{matrix}$.—Pinner does not mention this imido ester in his work "Die Imidoaether und ihre Derivate." We obtained it as a colorless, pleasant-smelling oil, which boiled unaltered at 115.5° at 12 mm. pressure, and at 232° at 765 mm. pressure.

	Calculated for $C_{10}H_{13}NO$.	Found.
N	8.59	8.59

The hydrochloride melts at 125°, giving off ethyl chloride and forming benzamide.

	Calculated for $C_{10}H_{13}NO.HCl$.	Found.
Cl	17.79	17.77

The picrate, obtained in the same manner as the corresponding methyl ester derivative, forms lemon-yellow prisms, which melt with charring at 261°, or 98° higher than the picrate of benzimidomethyl ester.

Acetylbenzimido(normal)propyl Ester, $C_6H_5C\begin{matrix}NCOCH_3\\ \diagup\\ \diagdown\\ OCH_2CH_2CH_3\end{matrix}$.—When acetyl chloride is added to the imido ester in ether the separation of hydrochloride begins at once. The mixture was allowed to stand twelve hours, the ether solution was shaken with dilute sodium hydrate, and, on drying and evaporating, an oil was obtained. This was distilled at 12 mm. pressure,

and the fraction boiling from 153°–160° was redistilled, when the main portion boiled at 153° at 13 mm. pressure. A nitrogen determination gave :

	Calculated for $C_{13}H_{19}NO_2$.	Found.
N	6.83	6.79

When this acyl imido ester is exposed to the air or treated with acids it deposits acetbenzamide.

Benzoylbenzimido(normal)propyl Ester, $C_6H_5C\begin{matrix}\diagup\!\!\diagup NCOC_6H_5\\ \diagdown\quad OCH_2CH_2CH_3\end{matrix}$.

This compound was obtained in the form of an oil which was distilled at 17 mm. pressure ; the portion boiling from 231°–232.5° was analyzed with the following result :

	Calculated for $C_{17}H_{17}NO_2$.	Found.
N	5.24	5.20

When treated with dilute hydrochloric acid it gave dibenzamide.

Benzimidoisobutyl Ester, $C_6H_5C\begin{matrix}\diagup\!\!\diagup NH\\ \diagdown\quad OC_4H_9\end{matrix}$.—Pinner found that when this imido ester is liberated from the hydrochloric acid salt, by means of ammonia, and then a distillation is attempted, it is largely decomposed. We have found that if it is liberated by means of a ten per cent. solution of ice-cold sodium hydroxide, and then distilled under diminished pressure, it can afterwards be distilled at ordinary pressures without the slightest decomposition. It was observed to boil at 9 mm. pressure at 117°.5 to 120°, and at ordinary pressure from 248°–250°. It gives an oily precipitate with alcoholic mercuric chloride, which finally solidifies.

Benzoylbenzimidoisobutyl Ester, $C_6H_5C\begin{matrix}\diagup\!\!\diagup NCOC_6H_5\\ \diagdown\quad OC_4H_9\end{matrix}$. — The product in this case was an oil which, when distilled at 15 mm. pressure, boiled from 228°–235°. The distillate easily solidified and, on crystallizing from ligroïn, it melted constantly at 54.5°.

	Calculated for $C_{18}H_{19}NO_2$.	Found.
N	4.9	4.9

Phenylacetimidomethyl Ester, $C_6H_5CH_2C(=NH)OCH_3$.–The hydrochloride of this imido ester was prepared by Pinner. He does not mention the free base. When prepared as stated in the case of benzimidoisobutyl ester, it gave a pleasant-smelling oil, which distilled at 114.5°–115° at 20 mm. pressure.

Phenylacetimidoethyl Ester, $C_6H_5CH_2C(=NH)OC_2H_5$. — It was found that this ester could be distilled under diminished pressure. It boiled at 116° at 15 mm. pressure. On attempting then to distil it at ordinary pressure it decomposed into alcohol and the nitrile.

Benzoylphenylacetimidoethyl Ester, $C_6H_5CH_2C(=NCOC_6H_5)OC_2H_5$. —This was obtained as an oil which did not solidify without decomposition. It boils from 215°–216° at 13 mm. pressure.

	Calculated for $C_{17}H_{17}NO_3$.	Found.
N	5.2	5.9

In one attempt to prepare the above, a mass of plates separated on evaporating the ether solution. These melted at 128° and contained 11.31 per cent. nitrogen; calculated for benzamide, 11.56. The compound, therefore, readily decomposes into benzamide and phenyl ethyl acetate. The above analyzed material evidently contained some benzamide, which explains the high result for nitrogen.

NEW HAVEN, November, 1897.

LVI.—NOTE ON DOUBLE SALTS OF THE ANILIDES WITH CUPROUS CHLORIDE AND CUPROUS BROMIDE.

By William J. Comstock.

In studying the behavior of certain "Schiff bases" toward cuprous chloride and cuprous bromide, it seemed to me desirable to find derivatives of the cuprous halides which should be soluble in organic solvents and give up the halides easily. In looking for such derivatives, I found the acetanilide salts here described. As the anilides enter so few combinations in which the basic character of the nitrogen appears, it seems worth while to show that acetanilide is not an exceptional case. The formyl compounds give similar double salts with the greatest ease, but the formyl group splits off so easily under the condition necessary for their formation, that accurate analytical results are difficult to obtain. For instance, when formanilide is added to a solution of cuprous bromide in a mixture of formic and hydrobromic acids, there is formed at once a salt crystallizing beautifully in well-developed, colorless, doubly-terminated prisms. On standing for but a few minutes at ordinary temperature, a change into small plates with very noticeable pearly luster, can be observed. These plates consist of the double salt of aniline with cuprous bromide, $C_6H_5NH_2HBrCuBr$. The corresponding salt of formparatoluide was, however, obtained, and gave on analysis sufficiently accurate results.

An interesting series of perhalides of the anilides has been carefully studied in this laboratory by Wheeler and Walden.[1] It will be seen that the salts here described,

$(Anilide)_2+HBr+CuBr$, and $(anilide)_2+HBr+2CuBr$,

correspond to two of the three types of perhalides obtained by the above-mentioned investigators.

Experimental.

$(C_6H_5NH.COCH_3)_2HClCuCl$.—An advantageous solution for the preparation of this salt consists of a mixture of one

[1] This Journal, 18, 85.

volume of glacial acetic acid, one volume of strong hydrochloric acid, and two volumes of water. The acetanilide and cuprous chloride are dissolved in the hot mixture in the proportion indicated in the above formula. On cooling, the solution solidifies to a mass of long, thin, white prisms. When freshly prepared and not quite dry, the salt dissolves easily in alcohol, crystallizing in beautiful, long prisms, when the hot concentrated solution is allowed to cool slowly. This complete solution in alcohol is doubtless due to the small quantity of hydrochloric acid which has not yet been removed, as the perfectly dry salt always leaves a small residue of cuprous chloride when treated with alcohol. However, many grams of the dried substance will form a clear solution in alcohol to which a few drops of dilute hydrochloric acid are added. Methyl alcohol and acetone can also be used for recrystallizing it. Protracted boiling of the solution splits off the acetyl group. The compound has no sharp melting-point. When heated slowly it darkens at about 140°; complete fusion, accompanied by violent decomposition, takes place near 170°. Freshly prepared it is entirely colorless, but it usually has a faint yellow color by the time it is dry, especially when prepared in quantity. When dry it is quite stable, and can be kept for months with no change of color, unless exposed to moist air. It does not lose hydrochloric acid *in vacuo* over potassium hydroxide, and when dry can be heated to 100° without loss of weight. The following analytical results were obtained:

	Calculated for above composition.	Found. I.	Found. II.
Cu	15.64	15.73	15.77
Cl	17.51	17.50	17.47

$(C_6H_5NHCOCH_3)_2HBr.CuBr$.—This salt can be prepared from its constituents by using a mixture of one volume glacial acetic acid, one volume hydrobromic acid (sp. gr. 1.49), and two volumes of water. More advantageous, however, is the preparation in alcoholic solution. The anilide and bromide are used in theoretical proportion, the hydrobromic acid in slight excess. Sufficient alcohol is used to effect complete solution at the boiling-point, and the hot solution cooled slowly. The salt separates in long, colorless, doubly-terminated prisms.

Similarly to the cuprous chloride salt, it dissolves completely in alcohol, methyl alcohol and acetone, if a drop of hydrobromic acid is added. While drying, the crystals show temporarily on the surface that purple color so characteristic of copper compounds in presence of strong hydrobromic acid; but when dry they have at most a light grayish color. The dried salt is fully as stable as the corresponding chloride. On heating, it begins to darken at about 170°, and melts with decomposition from 185° to 195°, according to the rapidity of heating. Analysis gave the following results:

	Calculated.	Found. I.	Found. II.
Cu	12.82	13.29	13.20
Br	32.36	32.39	32.41

$\left(C_6H_4\begin{matrix}Br\\ \diagup\\ \diagdown\\ NHCOCH_3\end{matrix}\right)_2HBrCuBr$.—Parabromacetanilide gives with cuprous bromide a double salt of the above composition. The compound separates in long, colorless prisms, on cooling a hot solution of the constituents dissolved in a mixture of two volumes of alcohol and one volume of hydrobromic acid (sp. gr. 1.49). The substance thus prepared and dried *in vacuo* over sulphuric acid and potassium hydroxide, was used for a copper estimation, which gave 9.79 per cent. copper. For the above composition the theory requires 9.72 per cent. copper.

Formparatoluide and Cuprous Bromide.

$\left(C_6H_4\begin{matrix}CH_3\\ \diagup\\ \diagdown\\ NHCHO\end{matrix}\right)_2HBr+2CuBr$.—This salt must be prepared in the cold and dried quickly. Three grams of formparatoluide dissolved in 12 cc. of formic acid (sp. gr. 1.20) were added to a solution of three grams of cuprous bromide dissolved in 24 cc. dilute hydrobromic acid (one volume HBr, sp. gr. 1.49, to one volume water). The salt separated at once in colorless, flat prisms. It was dried on a porous plate, then *in vacuo* over sulphuric acid and potassium hydroxide. It gave the following results on analysis:

	Calculated.	Found. I.	Found. II.
Cu	19.88	19.57	19.68
Br	37.63	37.47	....

ORGANIC CHEMISTRY FOR THE LABORATORY. By W. A. NOYES, PH.D., Professor of Chemistry in Rose Polytechnic Institute, Terre Haute, Indiana. Easton, Pa.: Chemical Publishing Co. 1897. 257 pp. Price $1.50.

In his preface, the author in speaking of the object of this book, says: "Two distinct purposes have been kept in view. The first has been to furnish the beginner with sufficiently full and accurate directions, and clear, concise theoretical explanations of processes which have been found successful in practical laboratory experience. The second object has been to furnish the more advanced student and practical worker with a guide which will aid him in the selection of processes which are likely to be successful for the preparation of compounds which he may desire to use.

"It is for this second reason particularly that the number of preparations given is considerably greater than it would be profitable for the average student to prepare, and that the references to the literature have been made quite full."

The book has some points of similarity with those of Levy, of Gattermann, and of E. Fischer, but, of course, it differs from these in some respects. It does not deal with general principles in the same way that Gattermann's book does, and it covers more ground than is covered either by Levy, or by Fischer.

The matter dealt with is classified as follows: In Chapter I, Acids are presented; in Chapter II, Derivatives of Acids; in Chapter III, Halogen Compounds; in Chapter IV, Nitro Compounds; in Chapter V, Amines; in Chapter VI, Hydrazo, Azo, Diazo Compounds, etc.; in Chapter VII, Alcohols and Phenols; in Chapter VIII, Aldehydes, Ketones, and their Derivatives; in Chapter IX, Sulphonic Acids and Sulphine Compounds; in Chapter X, Hydrocarbons; in Chapter XI, Miscellaneous Compounds; and in Chapter XII, Qualitative Examination of Compounds and Reagents.

The book is clearly written, and the directions appear to be in every way satisfactory. There is sufficient discussion of the reactions to make them clear, and to direct the attention of the student to their relations to other similar reactions. If a student should conscientiously work through the course here laid down, he could not fail to become familiar with most of the important reactions of organic chemistry. It would, however, be difficult for him under ordinary circumstances to make all these preparations, and, as has been seen, the author does not expect this. The book can be cordially

recommended to teachers and to students, and those who are engaged in teaching and studying organic chemistry will do well to consult it frequently. It may well take its place by the side of those other laboratory guides that we are constantly using, namely, Gattermann, Levy, and Fischer.

There is one point which ought to be noted, and that is the evident carelessness in the proof-reading, as shown particularly in the misspelling of proper names. As examples of this the following incomplete list is given: Page 18, "Papow" instead of "Popoff," and "Hill" instead of "Hell;" p. 51, "Rugheimer" instead of "Rügheimer;" p. 83, "v. Meyer" instead of "V. Meyer"; p. 89, "Wislecenus" instead of "Wislicenus;" p. 101, "Lanteman" instead of "Lautemann;" p. 123, "Hoffmann" instead of "Hofmann," and this well-known name is also misspelled on pages 133, 138, 141 and 147; p. 160, "Fisher" instead of "Fischer;" p. 221, "Hantsch" instead of "Hantzsch." I. R.

CALCIUMCARBID UND ACETYLEN IN VERGANGENHEIT, GEGENWART UND ZUKUNFT. Von D. JOVAN P. PANAOTOVIC. Leipzig: Barth. 1897. 125 pp. Price 3.60 marks.

Any one interested in acetylene,—and who is not?—will find this book of much interest. The author is a believer in the gas, and tries to show that there are good reasons for his faith. The history of calcium carbide is sketched, and the relation between the scientific work of Moissan and the technical work of Willson is fully discussed. The main points of Willson's patent are stated and then the author indulges in this pleasant fling at Americans: "Willson scheint, wie seine Landsleute es oft thun, gar nicht nach seinem patentirten Verfahren zu arbeiten." However, in general, full justice is done to Willson's work, and it is clearly recognized that the rapid development of the carbide industry is due to this work. The question of the cost of the carbide and of the relative cost of acetylene gas and ordinary illuminating gas, is gone into quite fully, and anyone interested in this question will find much information of value in the book.

The various uses to which acetylene has been put and for which it has been recommended are then taken up. Under the head of the poisonous properties of acetylene the author reaches the conclusions that the gas is not as poisonous as it is generally supposed to be, and that accidents can be prevented by care and attention. The acetylene explosions that have done so much to prejudice the world against the gas are discussed in detail, the evidence being given and the conclusions of the courts in important cases. It appears that these explosions were due to want of experience in dealing with the

apparatus, and that they were not of such a character as to justify the wide-spread prejudice. The author says: "In fact it is an easy matter to avoid the dangers by taking proper precautions."

A very curious application of the carbide and of acetylene has been suggested, but it does not seem probable that this application will be of any service to the world. The suggestion is that life-preservers be supplied with calcium carbide, and so arranged that water can gain access to the rings in which the carbide is placed. On being thrown into water, of course, the acetylene would be generated and the vessels filled with gas.

I. R.

MANUAL OF QUALITATIVE CHEMICAL ANALYSIS. By the late DR. C. REMIGIUS FRESENIUS, Privy Aulic Counsellor and Professor, Director of the Chemical Laboratory at Wiesbaden. Authorized Translation by HORACE L. WELLS, M.A., Professor of Analytical Chemistry and Metallurgy in the Sheffield Scientific School of Yale University. New Edition, Thoroughly Revised. From the Sixteenth German Edition. John Wiley and Sons: New York. 1897.

The works of Fresenius on analytical chemistry need no introduction; for, either in the original or in the form of a more or less faithful translation, they are known to all chemists, and probably the majority of chemists have found them indispensable in their practice. For fifty years or more they have easily maintained a leading position as guides in analytical work. As such they have served the practical chemist, the teacher, and in many laboratories the student also. Their influence upon the education of more than one generation of chemists has undoubtedly been very great, but whether that influence has been good or bad is a question which may well be raised. Their phenomenal success can hardly be regarded as proof positive that their influence is wholly beneficent, for chemists and students of chemistry, like others, work along the lines of least resistance; and with them, as with others, the popular tools are those which save labor and hard thinking. In the works of Fresenius a complex subject has been successfully reduced to a finished but highly mechanical art. This is their great merit and the cause of their universal currency. But it may well be asked whether, by relieving the worker, as they do, from the necessity of an extensive study of the general subject, of treasuring his individual experiences, and of constantly exercising his constructive powers, they have not exerted a disastrous influence upon the laboratory study of chemistry as a mental discipline.

The translation is an admirable one. H. N. M.

ELEMENTS OF CHEMISTRY. By RUFUS P. WILLIAMS, in charge of the Chemical Department of the English High School, Boston, and author of "Introduction to Chemical Science," "Chemical Experiments, General and Analytical," and "Laboratory Manual of Inorganic Chemistry." Boston and London: Ginn & Company. 1897. 412 pp. Price $1.20.

Here is another attempt to present the elements of chemistry to the beginner as they should be presented. The book is neatly gotten up, both as regards the type, paper, and illustrations. It has a fresh look about it, and will probably on this account attract the attention of teachers. There are a number of good features in the book, as there are in most books on the subject that have appeared within the last few years.

In addition to the descriptive part there are directions for a large number of experiments to be carried out in the laboratory, in accordance with the usage which is becoming general.

It is impossible to judge any book of this kind fairly without testing it with students, and therefore it is not the purpose of the writer of this notice to go into details on the subject of this particular book. The impression made upon the writer, in general, is that the speculative part is a little beyond the beginner, and that the effect of using such a book would be to give the student a wrong idea in regard to the relation between facts and theory. It would be interesting to hear the honest opinion of competent young students who study for the first time Chapter X, for example, on valence, in which he is given a definition of isomerism and views of structure, as illustrated by benzene, the familiar hexagon formula of which is exhibited. It is difficult enough for an advanced student to form a clear conception of the meaning of that and similar formulas, and in fact they are generally misunderstood. What service the presentation of these advanced ideas to the beginner can be, it is extremely difficult, not to say impossible, to see. Similarly, too much seems to be made of writing equations, as presented in Chapter XI. Equations are, of course, well enough in their way, and are of service to the chemist, but if their importance is magnified in the lower stages of the course, the student is pretty sure to get the idea that writing equations is chemistry. Other comments of a similar kind might be made in regard to other parts of the book, and the general statement may be made that it is doubtful whether this book will be of much assistance in improving the methods of teaching chemistry. I. R.

THE DEVELOPMENT OF THE PERIODIC LAW. By F. P. VENABLE, PHD., F.C.S., Professor in the University of North Carolina. Easton, Pa.: Chemical Publishing Company. 1896. pp. 322. Price $2.50.

This book is the result of a conscientious effort on the part of the author to bring together the scattered literature on the subject of the Periodic Law, and as such it will be welcome to chemists everywhere. The importance of the Periodic Law is coming to be recognized more and more clearly year by year, and the law is coming to be used more and more as the basis of a scientific treatment of the facts of chemistry. It is therefore desirable that all chemists should have the opportunity to familiarize themselves with the development of our knowledge on the subject of the Law, and Professor Venable has done us a good service in pointing out the sources of information and giving us an idea of the contents of important articles that have a bearing upon this subject.

Probably all chemists will be surprised to learn how much has been written on the subject of regularities between the atomic weights or equivalent numbers. The author calls attention to the fact that "Before the atomic theory was formulated, numerical relations were proposed by Richter, the founder of Stoichiometry, between the equivalents obtained by him for the various bases and acids. This mathematical work of his served but little purpose beyond bringing the whole subject of his equivalents into some disrepute;" that after Prout, in 1815, pointed out the strange fact of the close approximation of the atomic weights to whole numbers, the so-called "Multiplenfieber" took possession of the chemical world. Then, through a series of years, Berzelius, Döbereiner, Turner, Penny, Meinicke, Dumas, Faraday, Kremers, Gladstone, Cooke, Kotikovsky, Lennsen, Newlands and many others, made suggestions bearing upon the regularities which were first clearly pointed out in a broad way by Lothar Meyer, and by Mendeléeff in 1869.

The history of the Periodic Law since that time is fairly familiar to most chemists, though it will again astonish many to find how many suggestions have been made during the past thirty years.

The reading of this book can be recommended to all chemists. It is interesting and instructive, and its study should be of assistance in causing the development of a more scientific habit than that which frequently characterizes chemists in their dealings with chemical facts.

The text is illustrated by a number of figures taken from original articles, and no pains have been spared to treat the subject in a clear and satisfactory manner. I. R.

A COURSE OF PRACTICAL CHEMISTRY. By M. M. PATTISON MUIR, M.A. Fellow and Prælector of Chemistry in Gonville and Caius College, Cambridge. Part I.—Elementary. Longmans, Green & Co., London, New York and Bombay. 1897. 319 pp. Price 4s, 6d.

Mr. Muir has long been known as an earnest thinker and worker in the field of chemistry, and he has been trying, further, to improve the methods of teaching, his main effort being directed towards a more philosophical treatment of the subject than it commonly receives. There is no doubt that the presentation of the facts and principles of chemistry is generally scrappy and unsatisfactory, and many teachers are anxiously awaiting something better than they have at present in the way of a laboratory guide and text-book.

Mr. Muir, in his preface, says: "This book is offered to students and teachers as the first part of what I hope may prove to be a tolerably satisfactory and fairly systematic course of practical chemistry. It is the first portion of the result of very many attempts made during twenty-five years to devise a workable system of teaching in the laboratory."

This part is divided into three sections: Section I has to do with Experiments and Chemical Change; Preparations of Various Compounds, Reactions of Acids, Alkalies, and Salts. Section II deals with Volumetric Estimations of Acids, Alkalies, Alkali Carbonates, Iron Salts, Chlorites, Calcium Compounds, and Iodine. Section III deals with Qualitative Analysis. The experiments described in the first four lessons need no special comment, as they are quite familiar and are utilized in many laboratory guides. In Lesson V, the matter of which is described thus, "Not-Mixtures divided into Compounds and Elements, Two Kinds of Chemical Changes—Building up and Breaking up," the experiments given are on the burning of magnesium in the air, the heating of lead in air, and the effect of heat on burnt mercury. These experiments are intended to show the student that the air takes part in the changes which are the subject of study; and then in Lessons VII, VIII and IX a somewhat elaborate study of the Rusting of Iron is taken up. The underlying thought of these lessons is clear and logical, but it seems to the writer of this notice that the experiments are not well chosen. The rusting of iron is an extremely complex process, the nature of which we do not yet fully understand, but so far as it has been studied it is certain that it involves not only the action of the water and oxygen, but that of carbon dioxide upon the iron, and the kind of study that the beginner can give to the phenomenon is not such as to leave clear impressions upon his mind.

The same criticism can be made of several other experiments described in the book. While there is much to commend in the course laid down by Mr. Muir, it is questionable whether the course as a whole will give more satisfactory results than some of those which are now followed. Section I is the only one that calls for any comment, for in Section II we have to deal with familiar Volumetric Estimations, and in Section III Qualitative Analysis, and under neither of these heads is there likely to be much originality in the presentation. I. R.

AN INTRODUCTORY COURSE IN QUANTITATIVE CHEMICAL ANALYSIS. By PERCY NORTON EVANS, PH.D., Associated Professor of Chemistry, Purdue University, LaFayette, Indiana. Boston and London: Ginn & Company, Publishers. 1897. 84 pp.

This little book is intended to assist teachers and students in dealing with the subject of Quantitative Analysis. After a brief introduction, in which the processes of weighing, filtering, and washing are briefly referred to, directions are given for the estimation of a number of elements and groups, as for example: Aluminium in alum, copper in copper sulphate, calcium in calcium carbonate, sulphuric acid in copper sulphate, chlorine in potassium chloride, phosphoric acid in sodium phosphate, potassium in potassium chloride, etc.

The course laid out is sufficiently full for the average student of chemistry, though hardly full enough for an advanced student who is looking forward to chemistry as his life work. The directions are clear and accurate, and the book ought to prove useful to those for whom it is intended. I. R.

TAFELN UND TABELLEN ZUR DARSTELLUNG DER ERGEBNISSE SPEKTROSKOPISCHER UND SPEKTROPHOTOMETRISCHER BEOBACHTUNGEN. Herausgegeben von TH. W. ENGELMANN. Leipzig: Verlag von Wilhelm Engelmann. 1897.

This publication consists of two charts, with tables to accompany them, which are especially designed to render easy the recording of absorption-spectra and of photometric observations on them.

Plate I has along its upper edge a continuous prismatic spectrum with the principal solar lines, A, B, C, recorded on them. It also contains across the page other continuous spectra, forming colored backgrounds, on which the absorption-spectra of any substance can be at once recorded from the observations made by the spectroscope. In this way, on the same page, the absorption spectra of various substances may be recorded, or the changes in the spectra of any one substance may be noted.

Plate II contains along its upper edge a similar prismatic

spectrum, while the rest of the sheet is so arranged with lines vertical and horizontal, as to render it easy to make certain records of photometric observations or calculations corresponding to particular wave-lengths. In the tables which accompany these plates there are full directions as to their use and descriptions of various purposes for which they can be used. The Mathematical Tables are particularly designed to render easy any calculations and make it possible to record on the plate in suitable places those physical or chemical quantities which are most important and which are desired for further study. Among these quantities it may be well to mention :

First, the directly measured intensity of the transmitted light corresponding to different wave-lengths when the light has passed through various layers or various concentrations of coloring matter.

Second, the "extinction coefficients," which may be calculated from these observations by means of the tables.

Third, the comparison between actual observed intensities and those calculated from other observations.

There are other uses to which these plates and tables may be put, and they will undoubtedly prove of great value to both chemists and physicists. To students in physical laboratories they furnish what has long been needed, a simple prismatic chart on which can be recorded not alone absorption-spectra, but also emission-spectra and the bands which are obtained by absorption through quartz and other substances where the rotation of the plane of polarization is to be studied.

J. S. A.

THE PRINCIPLES OF MATHEMATICAL CHEMISTRY. THE ENERGETICS OF CHEMICAL PHENOMENA. By DR. GEORG HELM, Professor in the Royal Technical High School, Dresden. Authorized Translation from the German, by J. LIVINGSTON R. MORGAN, PH.D. (Leipzig), Instructor in the Brooklyn Polytechnic Institute. John Wiley & Sons: New York; Chapman & Hall: London. 1897. pp. 228.

The rapid increase in the number of American and English students of physical chemistry has created a demand for an English version of this excellent work by Helm. When a student tries to read a book in a language with which he is not very familiar, upon a difficult subject, his energies are of necessity divided, and the result is not always entirely satisfactory. It may justly be claimed that the student should familiarize himself with the language, but, as this cannot be done in a day, we must meet the case as it is, rather than as it should be.

In order that a translation should be successful, it must, above all, be true to the original, and should, at the same

time, be expressed in clear, if not elegant, language. That the translation in hand always meets these demands satisfactorily cannot be maintained.

On page 15, we read: "Therefore thermochemical equations, strictly considered, should be given not only in a special chemical state, but also in a special physical one," as the translation of "Daher muss in den thermochemischen Gleichungen, streng genommen, nicht nur der chemische, sondern auch der besondere physikalische Zustand angegeben werden." On page 19, we find this statement: "Although heat is the form of energy which is produced in the greatest amount by the chemical energy differences." The German bears no direct relation to this: "Wenn auch die Wärme diejenige Form der Energie ist in der die chemischen Energieunterschiede vorwiegend gemessen werden." We find on page 41, "They were, however, investigated in different ways;" while the original says: "Beide sind aber in sehr verschiedenem Masse der Untersuchung unterworfen worden."

A statement is made on page 78, which is not only erroneous, but the English is almost unintelligible. "If, however, only one phase is present, then the other can only appear when it has *not a smaller chemical intensity* than the other." The German is perfectly clear: "Ist aber nur eine der Phasen vorhanden, so kann der andere nur auftreten *wenn sie kleinere chemische Intensität hat*."

If such discrepancies as these come out as the result of a comparison of a few paragraphs of the English, with the original, it is to be feared that the translation, in other places, is not all that could be desired.

While it is true that the translation of a technical mathematical work, like the one under consideration, is not a simple task, yet it does seem that we could reasonably demand a better product than has been furnished. HARRY C. JONES.

CORRECTION.

Vol. **19**, p. 891, line 17 from bottom: *for* "lead" *read* "lead oxide."